A GENERAL KINETIC MODEL FOR EPOXY POLYMERIZATION

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in Partial Fulfillment of the Requirements

for the Degree of

Master of Technology

by

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to the

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

June 1997

Dedicated To...

...My Loving Parents

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CERTIFICATE

This is to certify that the work contained in this thesis, entitled **A General Kinetic Model for epoxy Polymerization** has been carried out by **Sasanka Raha** under my supervision and this work has not been submitted elsewhere for a degree.

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Nomenclature

AA_n, AB_n,... , FF_n,	Molecular species defined in Table 2
A	Hydroxyl end group
AA_0	Bisphenol A (monomer)
B	Sodium phenoxide end group
DGEBPA	Diglycidyl ether of bisphenol A
E	Glycidyl ether group, Objective function
EP	Epichlorohydrin
F	Chlorohydrin end group
k_i	Rate constant for the ith reaction ($m^3\ mol^{-1}\ hr^{-1}$)
M_n	Number average molecular weight
M_w	Weight average molecular weight
M_j	Molecular Mass of jth species
$N_{j,exp}$	Number of experimental data points available for the jth species
PDI	Polydispersity index
t	Time (hr)
W_j	Weightage factor assigned to the experimental data set for the jth oligomer, or summation of oligomers

Greek letter

$\lambda_j^{\ k}$	kth moment of the jth species as given in Table 3, k=0,1,2

Subscripts/superscripts

exp	Experimental value
0	Initial value
theor	Theoretical value

Symbol

[ ]	Concentration (mol/m^3)

Abstract

A general kinetic framework to study epoxy polymerization is developed. Best-fit values of five rate constants are obtained using some experimental chromatographic data available in the open literature on a few low molecular weight molecular species. Detailed sensitivity studies are then carried out to identify the most important rate constants. Average molecular weights and the polydispersity index are predicted using these parameters. The present work is more general than earlier kinetic models, and does not have the drawbacks of the probabilistic models available in the open literature. It can easily be extended to model industrial reactors.

Chapter 1

Introduction

Epoxy polymers are formed by the reaction of an epoxy group ( ) with a hydroxyl group. These resins are manufactured using two common processes, the taffy process and the advancement process, but adaptations of these are not uncommon. In the taffy process, a diol, such as bisphenol A [HO– R– OH, where R is C_6H_5– $C(CH_3)_2$– C_6H_5] is reacted with a controlled excess of epichlorohydrin (CH_2CHCH_2Cl) give a mixture of low molecular weight oligomers having glycidyl ether groups (–OCH_2CHCH_2) at both ends. The lowest molecular weight oligomeric product is referred to as the diglycidyl ether of bisphenol A (DGEBPA). This process is carried out under the catalytic influence of an alkali such as sodium hydroxide. Water is present in the heterogeneous reaction mass, and it is claimed[1] that the reaction takes place at the water/organic-medium interface. In the advancement process, bisphenol A is reacted with equimolar amounts of commercially available DGEBPA. This is a typical AA + BB step growth polymerization,[2,3] in which complications are introduced by the presence of (over 10% of) impurities, e.g., higher molecular weight diepoxides, monofunctional epoxides, etc.[4,5] Yet another process[5] involves the addition of bisphenol A to a solution of epichlorohydrin in a solvent (e.g., methyl cellosolve). Pulverized sodium hydroxide is added to this reaction mass in a controlled manner over a period of time. A specified

temperature history is effected and intermediate washing with water and distillation under reduced pressure are used to give the final resin.

It is clear that a variety of physico-chemical phenomena are associated with the polymerization of epoxy resins in an industrial reactor. These are quite complex and there is a definite need to study several of the interesting aspects of these polymerizations. Indeed, very few experimental or theoretical studies are available in the open literature on the modeling of *industrial* epoxy reactors.[5-7] This work intends to fill this gap to a small extent and attempts to provide a general mathematical framework for the study of the kinetics of the reactions. Limitations posed by heat and mass transfer effects can be incorporated subsequently, in order to develop a comprehensive reactor model.

The first systematic study of the kinetics of epoxy polymerization was done by Batzer and Zahir.[1,8-10] These workers have reported both experimental and theoretical work on the molecular weight distribution of epoxy resins. Their work was based on Flory's statistical method,[2,3] which, in turn, assumes equal reactivity of the functional groups. Deviations of experimental results from theory have been explained due to[8,9] the presence of monofunctional epoxides in the resin and the possibility of branching reactions. These workers conclude that the reactivity of epichlorohydrin with the phenolic hydroxyl group is higher than with the aryl glycidyl ether group.

Ravindranath and Gandhi[4] improved the theoretical model developed by Batzer and Zahir and considered the unequal reactivity of epoxide groups. They used the probabilistic technique developed by Case[11] and observed improved agreement between model predictions and some of the experimental results of Batzer and Zahir. However, their model had two major drawbacks. It is well known that the alkali has a

very important role to play in determining the molecular weight distribution (MWD) of the product. Since alkali leads to the production of phenoxide ions,[1] it is possible to have some degree of control over the concentration of the phenoxide anion by controlling the rate of intermediate addition of the alkali. This enables one to alter the MWD of the resin. Unfortunately, the effect of alkali addition on the MWD is not considered by Ravindranath and Gandhi. In addition, in their model, one of the intermediate reactions (dehydrochlorination) has been considered to be extremely fast and hence the concentration of the chlorohydrin species is zero . This is contrary to the experimental observations of Batzer and Zahir,[8] who do observe this species in their GPC studies. Moreover, the use of the probabilistic approach by Ravindranath and Gandhi[4] prevents its use in modeling industrial epoxy reactors which are often operated in the semibatch mode (with intermediate addition of sodium hydroxide and vaporization of the volatiles). This study attempts to overcome these drawbacks, and presents a general *kinetic* framework, which can easily be adapted subsequently to incorporate several important physico-chemical phenomena which are often present in industrial reactors.

Chapter 2

Formulation

Any attempt to develop a mathematical model to describe the performance of an industrial semibatch epoxy reactor should first focus attention on the kinetics of the reaction, unencumbered by other influences. The detailed kinetic scheme[1,5] for epoxy polymerization incorporating most of the important reactions is shown in Table 1. The different end groups, -A,-B,-E and -F, are defined in this table. This scheme is more detailed than that used by Ravindranath and Gandhi[4] and takes care of the major weaknesses of their model, as described earlier. A study of the several reviews[5-7] in the open literature suggests that the scheme in Table 1 is fairly general, and so should be a good starting point for the study of epoxy reactors.

The various molecular species including the monomers present in the reaction mass at any time, are shown in Table 2. AA_0 represents one of the monomers, bisphenol A, while EP represents the other monomer. This kind of description is required in order to have correspondence with the kinetic scheme of Table 1. Table 2 also gives the molecular masses of all these species (for use in the computation of average molecular weights).

The kth moments (k=0,1,2,...) of the molecular species are defined in Table 3. It is necessary to use $(n+1)^k$ as the factor with the concentration, $[i_n]$, of any species of 'length' n to avoid giving zero weightage to the smallest species. The number and weight average molecular weights, M_n and M_w , for this system have been obtained starting from the fundamental equations[2,3]

Table 1
Reaction Scheme for Epoxy Polymerization

1. $\text{—OH} + \text{NaOH} \xrightarrow{k_1} \text{—ONa} + H_2O$

$\text{—A} + \text{NaOH} \xrightarrow{k_1} \text{—B} + W$

2. $\text{—ONa} + CH_2CHCH_2Cl \xrightarrow{k_2/H_2O} \text{—}OCH_2CHCH_2Cl + \text{NaOH}$ (O; OH)

$\text{—B} + \text{EP} \xrightarrow{k_2/H_2O} \text{—F} + \text{NaOH}$

3. $\text{—}OCH_2CHCH_2Cl + \text{NaOH} \xrightarrow{k_3} \text{—}OCH_2CHCH_2 + NaCl + H_2O$ (OH; O)

$\text{—F} + \text{NaOH} \xrightarrow{k_3} \text{—E} + NaCl + H_2O$

4. $\text{—ONa} + CH_2CHCH_2O\text{—} \xrightarrow{k_4/H_2O} \text{—}OCH_2CHCH_2O\text{—} + \text{NaOH}$ (O; OH)

$\text{—B} + \text{E—} \xrightarrow{k_4/H_2O} \text{—(BE)—} + \text{NaOH}$

5. $\text{—ONa} + ClCH_2CHCH_2O\text{—} \xrightarrow{k_5} \text{—}OCH_2CHCH_2O\text{—} + \text{NaOH}$ (OH; OH)

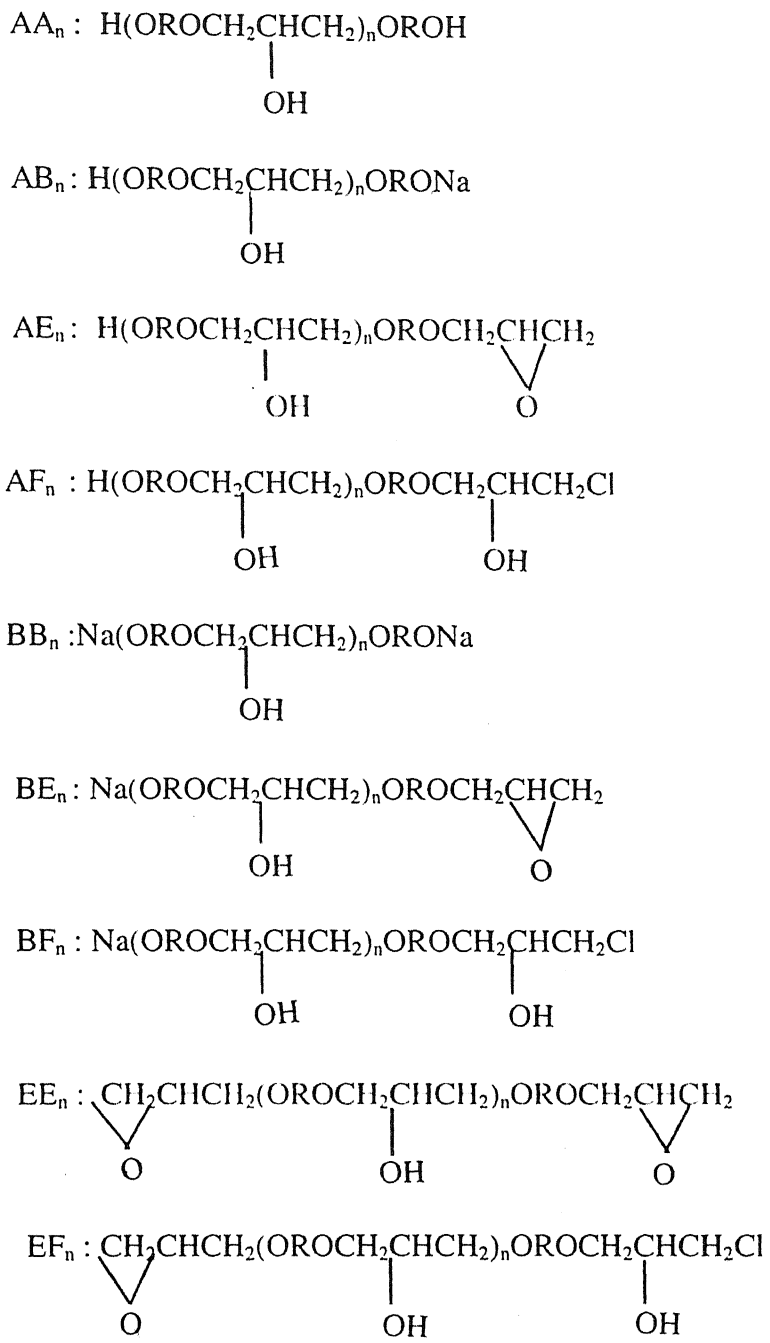
$\text{—B} + \text{—F} \xrightarrow{k_5} \text{—(BF)—} + \text{NaOH}$

End Groups Present in the Reaction Mass

—A	—OH
—B	—ONa
—E	$-CH_2CHCH_2$ (O)
—F	$-OCH_2CHOHCH_2Cl$

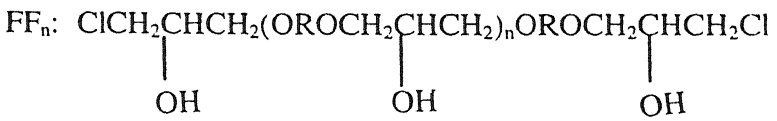
Table 2

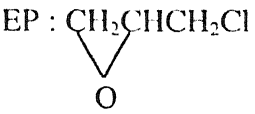
Different Molecular(Polymeric/Monomeric) Species Present in the Reaction Mass and Their Molecular Weights



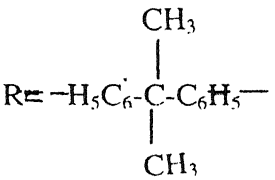
(Table 2 Continued ... a)

Table 2 (Continued...a)





where,



n=0,1,2,... for all cases

(Table 2 Continued... c)

Table 2 (Continued ... c)

Molecular Weights of Different Species

$$M_{AAn} = (n+1)(M_{AA0} + M_{EP} - M_{HCl}) - M_{EP} + M_{HCl}$$

$$M_{ABn} = n(M_{AA0} + M_{EP} - M_{HCl}) + M_{AB0}$$

$$M_{AEn} = (n+1)(M_{AA0} + M_{EP} - M_{HCl})$$

$$M_{AFn} = (n+1)(M_{AA0} + M_{EP} - M_{HCl}) + M_{HCl}$$

$$M_{BBn} = n(M_{AA0} + M_{EP} - M_{HCl}) + M_{BB0}$$

$$M_{BEn} = (n+1)(M_{AA0} + M_{EP} - M_{HCl}) + M_{AB0} - M_{AA0}$$

$$M_{BFn} = n(M_{AA0} + M_{EP} - M_{HCl}) + M_{AB0} + M_{EP}$$

$$M_{EEn} = (n+1)(M_{AA0} + M_{EP} - M_{HCl}) + M_{EP} - M_{HCl}$$

$$M_{EFn} = (n+1)(M_{AA0} + M_{EP} - M_{HCl}) + M_{EP}$$

$$M_{FFn} = (n+1)(M_{AA0} + M_{EP} - M_{HCl}) + M_{EP} - M_{HCl}$$

---

where,

n=0,1,2,... for all cases

M_{AA0} = molecular weight of bisphenolA

M_{EP} = molecular weight of epichlorohydrin

M_{HCl} = molecular weight of hydrochloric acid

Table 3

k^{th} Moments of Various Molecular Species

$$\lambda^k{}_{AA} = \sum_{n=0}^{\infty}(n+1)^k[AA_n]$$

$$\lambda^k{}_{AB} = \sum_{n=0}^{\infty}(n+1)^k[AB_n]$$

$$\lambda^k{}_{AE} = \sum_{n=0}^{\infty}(n+1)^k[AE_n]$$

$$\lambda^k{}_{AF} = \sum_{n=0}^{\infty}(n+1)^k[AF_n]$$

$$\lambda^k{}_{BB} = \sum_{n=0}^{\infty}(n+1)^k[BB_n]$$

$$\lambda^k{}_{BE} = \sum_{n=0}^{\infty}(n+1)^k[BE_n]$$

$$\lambda^k{}_{BF} = \sum_{n=0}^{\infty}(n+1)^k[BF_n]$$

$$\lambda^k{}_{EE} = \sum_{n=0}^{\infty}(n+1)^k[EE_n]$$

$$\lambda^k{}_{EF} = \sum_{n=0}^{\infty}(n+1)^k[EF_n]$$

$$\lambda^k{}_{FF} = \sum_{n=0}^{\infty}(n+1)^k[FF_n]$$

---

where,

k=0,1,2,...

(Table 3 continued... a)

Table 3 (Continued... a)

Average Molecular Weights

$$M_n = \frac{[\{M_{AA0} + M_{EP} - M_{HCl}\}\{\lambda^1_{AA} + \lambda^1_{AB} + \lambda^1_{AE} + \lambda^1_{AF} + \lambda^1_{BB} + \lambda^1_{BE} + \lambda^1_{BF} + \lambda^1_{EE} + \lambda^1_{EF} + \lambda^1_{FF} - \lambda^0_{AB} - \lambda^0_{BB} - \lambda^0_{BF}\} + M_{EP}\{\lambda^0_{EE} + \lambda^0_{FF} + \lambda^0_{EF} + \lambda^0_{BF} - \lambda^0_{AA} + [EP]\delta_{m0}\} + M_{HCl}\{\lambda^0_{FF} + \lambda^0_{AA} + \lambda^0_{AF} - \lambda^0_{EE}\} + M_{AB0}\{\lambda^0_{AB} + \lambda^0_{BE} + \lambda^0_{BF}\} - M_{AA0}\lambda^0_{BE} + M_{BB0}\lambda^0_{BB}]}{\{\lambda^0_{AA} + \lambda^0_{AB} + \lambda^0_{AE} + \lambda^0_{AF} + \lambda^0_{BB} + \lambda^0_{BE} + \lambda^0_{BF} + \lambda^0_{EE} + \lambda^0_{EF} + \lambda^0_{FF} + [EP]\delta_{m0}\}}$$

$$M_w = \frac{[\{M_{AA0} + M_{EP} - M_{HCl}\}^2\{\lambda^2_{AA} + \lambda^2_{AB} + \lambda^2_{AE} + \lambda^2_{AF} + \lambda^2_{BB} + \lambda^2_{BE} + \lambda^2_{BF} + \lambda^2_{EE} + \lambda^2_{EF} + \lambda^2_{FF}\} + 2\{M_{AA0} + M_{EP} - M_{HCl}\}\{(M_{HCl} - M_{EP})\lambda^1_{AA} + (M_{AB0} + M_{HCl} - M_{AA0} - M_{EP})\lambda^1_{AB} + M_{HCl}\lambda^1_{AF} + (M_{BB0} + M_{HCl} - M_{AA0} - M_{EP})\lambda^1_{BB} + (M_{AB0} - M_{AA0})\lambda^1_{BE} + (M_{EP} + M_{HCl} + M_{AB0} - M_{AA0} - M_{EP})\lambda^1_{BF} + (M_{EP} - M_{HCl})\lambda^1_{EE} + M_{EP}\lambda^1_{EF} + (M_{EP} + M_{HCl})\lambda^1_{FF}\} + (M_{EP} - M_{HCl})^2(\lambda^0_{AA} + \lambda^0_{EE}) + (M_{AB0} + M_{HCl} - M_{AA0} - M_{EP})^2\lambda^0_{AB} + M_{HCl}{}^2\lambda^0_{AF} + (M_{BB0} + M_{HCl} - M_{AA0} - M_{EP})^2\lambda^0_{BB} + (M_{AB0} - M_{AA0})^2\lambda^0_{BE} + (M_{EP} + M_{HCl} + M_{AB0} - M_{AA0} - M_{EP})\lambda^0_{BF} + M_{EP}{}^2\lambda^0_{EF} + (M_{EP} + M_{HCl})^2\lambda^0_{FF} + [EP]M^2_{EP}\delta_{m0}]}{[\{M_{AA0} + M_{EP} - M_{HCl}\}\{\lambda^1_{AA} + \lambda^1_{AB} + \lambda^1_{AE} + \lambda^1_{AF} + \lambda^1_{BB} + \lambda^1_{BE} + \lambda^1_{BF} + \lambda^1_{EE} + \lambda^1_{EF} + \lambda^1_{FF} - \lambda^0_{AB} - \lambda^0_{BB} - \lambda^0_{BF}\} + M_{EP}\{\lambda^0_{EE} + \lambda^0_{FF} + \lambda^0_{EF} + \lambda^0_{BF} - \lambda^0_{AA} + [EP]\delta_{m0}\} + M_{HCl}\{\lambda^0_{FF} + \lambda^0_{AA} + \lambda^0_{AF} - \lambda^0_{EE}\} + M_{AB0}\{\lambda^0_{AB} + \lambda^0_{BE} \lambda^0_{BF}\} - M_{AA0}\lambda^0_{BE} + M_{BB0}\lambda^0_{BB}]}$$

$$PDI = \frac{M_w}{M_n}$$

where,

δ_{m0} =0 for molecular weight determination without epichlorohydrin

=1 for molecular weight determination with epichlorohydrin

$$M_n = \sum_{\text{all species}} (\text{number fraction of } i^{th} \text{ species}) \times (\text{molecular weight of } i^{th} \text{ species}) \quad (1)$$

$$M_w = \sum_{\text{all species}} (\text{mass fraction of } i^{th} \text{ species}) \times (\text{molecular weight of } i^{th} \text{ species}) \quad (2)$$

The final expressions for these are also given in Table 3. Two sets of average molecular weights have been described. In one, the contribution of the epichlorohydrin is incorporated, while in the other, this is excluded from the computation. The latter is more appropriate and useful since experimental measurement of average molecular weights is usually performed after distilling out most of the epichlorohydrin from the reaction mass (there is negligible bisphenol A after some reaction has occured).

The mole balance equations for a well mixed *batch reactor* for the various species shown in Table 2 can easily be written, and are shown in Table 4. In these equations, extreme caution has been taken to account for all the possible formation and consumption terms of the individual molecular species. The detailed reactions between the several molecular species required to develop the equations in Table 4, are given in the Appendix (Table A-1). The mass balance equations in Table 4 can be summed up analytically (using the definitions in Table 3) to give the ordinary differential equations (ODEs) for the several moments (k=0,1 and 2). These are given in Table 5. The concentrations of the four end groups can be written in terms of the concentrations of the individual molecular species. These are given in Table 6. Mole balance equations for the various end groups and for some of the lower molecular weight oligomers (for which experimental data[1] are

Table 4

Mass Balance Equations for The Molecular Species

$$\frac{d[AA_m]}{dt} = -2k_1[AA_m][NaOH] + k_4\{\sum_{i=0}^{m-1}[AB_i][AE_{m-1-i}]\}\delta_{m0} + k_5\{\sum_{i=0}^{m-1}[AB_i][AF_{m-1-i}]\}\delta_{m0}$$

$$\frac{d[AB_m]}{dt} = k_1[NaOH]\{2[AA_m]-[AB_m]\} - k_2[AB_m][EP] - k_4[AB_m]\{\sum_{n=0}^{\infty}\{[AE_n]+[BE_n]+2[EE_n]+[EF_n]\}$$
$$- k_5[AB_m]\{\sum_{n=0}^{\infty}\{[AF_n]+[BF_n]+[EF_n]+2[FF_n]\} + \{2k_4\sum_{i=0}^{m-1}[BB_i][AE_{m-1-i}] + k_4\sum_{i=0}^{m-1}[AB_i][BE_{m-1-i}]$$
$$+ 2k_5\sum_{i=0}^{m-1}[AB_i][BF_{m-i-1}] + 2k_5\sum_{i=0}^{m-1}[BB_i][AF_{m-i-1}]\}\delta_{m0}$$

$$\frac{d[AE_m]}{dt} = -k_1[AE_m][NaOH] + k_3[AF_m][NaOH] - k_4[AE_m]\{\sum_{n=0}^{\infty}\{[AB_n]+[BE_n]+2[BB_n]+[BF_n]\}$$
$$+ \{k_4\sum_{i=0}^{m-1}[BE_i][AE_{m-i-1}] + 2k_4\sum_{i=0}^{m-1}[AB_i][EE_{m-i-1}] + k_5\sum_{i=0}^{m-1}[BE_i][AF_{m-i-1}] + k_5\sum_{i=0}^{m-1}[AB_i][EF_{m-i-1}]\}\delta_{m0}$$

$$\frac{d[AF_m]}{dt} = -k_1[AF_m][NaOH] + k_2[AB_m][EP] - k_3[AF_m][NaOH] - k_5[AF_m]\{\sum_{n=0}^{\infty}\{[AB_n]+[BE_n]$$
$$+ 2[BB_n]+[BF_n]\} + \{k_4\sum_{i=0}^{m-1}[BF_i][AE_{m-i-1}] + k_4\sum_{i=0}^{m-1}[AB_i][EE_{m-i-1}] + k_5\sum_{i=0}^{m-1}[BF_i][AF_{m-i-1}]$$
$$+ 2k_5\sum_{i=0}^{m-1}[AB_i][FF_{m-i-1}]\}\delta_{m0}$$

$$\frac{d[BB_m]}{dt} = k_1[AB_m][NaOH] - 2k_2[BB_m][EP] - 2k_4[BB_m]\{\sum_{n=0}^{\infty}\{[AE_n]+[BE_n]+2[EE_n]+[EF_n]\}$$
$$- 2k_5[BB_m]\{\sum_{n=0}^{\infty}\{[AF_n]+[BF_n]+2[FF_n]+[EF_n]\} + \{2k_4\sum_{i=0}^{m-1}[BB_i][BE_{m-i-1}] + 2k_5\sum_{i=0}^{m-1}[BB_i][BE_{m-i-1}]\}\delta_{m0}$$

$$\frac{d[BE_m]}{dt} = k_1[AE_m][NaOH] - k_2[BE_m][EP] + k_3[BF_m][NaOH] - k_4[BE_m]\{\sum_{n=0}^{\infty}\{[AE_n]+[AB_n]$$
$$+ 2[BB_n]+2[BE_n]+[BF_n]+2[EE_n]+[EF_n]\} - k_5[BE_m]\{\sum_{n=0}^{\infty}\{[AF_n]+[BF_n]+[EF_n]+2[FF_n]\}$$
$$+ \{k_4\sum_{i=0}^{m-1}[BE_i][BE_{m-i-1}] + 4k_4\sum_{i=0}^{m-1}[BB_i][EE_{m-i-1}] + k_5\sum_{i=0}^{m-1}[BE_i][BF_{m-i-1}] + 2k_5\sum_{i=0}^{m-1}[BB_i][EF_{m-i-1}]\}\delta_{m0}$$

(Table 4 Continued ... a)

$$\frac{d[BF_m]}{dt} = k_1[AF_m][NaOH] + 2k_2[BB_m][EP] - k_2[BF_m][EP] - k_3[BF_m][NaOH] - k_4[BF_m]\{\sum_{n=0}^{\infty}[AE_n] + [BE]_n + 2[EE_n] + [EF_n]\} - k_5[BF_m]\{\sum_{n=0}^{\infty}\{[AF_n] + [AB_n] + [BE_n] + 2[BB_n] + 2[BF_n] + [EF_n] + 2[FF_n]\} + \{k_4\sum_{i=0}^{m-1}[BF_i][BE_{m-i-1}] + 2k_4\sum_{i=0}^{m-1}[BB_i][EF_{m-i-1}] + k_5\sum_{i=0}^{m-1}[BF_i][BF_{m-i-1}] + 4k_5\sum_{i=0}^{m-1}[BB_i][FF_{m-i-1}]\}\delta_{m0}$$

$$\frac{d[EE_m]}{dt} = k_3[EF_m][NaOH] - 2k_4[EE_m]\{\sum_{n=0}^{\infty}\{[AB_n] + [BE_n] + 2[BB_n] + [BF_n]\} + \{2k_4\sum_{i=0}^{m-1}[BE_i][EE_{m-i-1}] + k_5\sum_{i=0}^{m-1}[BE_i][EF_{m-i-1}]\}\delta_{m0}$$

$$\frac{d[EF_m]}{dt} = -k_3[EF_m][NaOH] + k_2[BE_m][EP] + 2k_3[FF_m][NaOH] - k_4[EF_m]\{\sum_{n=0}^{\infty}\{[AB_n] + 2[BB_n] + [BE_n] + [BF_n]\} - k_5[EF_m]\{\sum_{n=0}^{\infty}\{[AB_n] + 2[BB_n] + [BE_n] + [BF_n]\} + \{2k_4\sum_{i=0}^{m-1}[BF_i][EE_{m-i-1}] + k_4\sum_{i=0}^{m-1}[BE_i][EF_{m-i-1}] + k_5\sum_{i=0}^{m-1}[BF_i][EF_{m-i-1}] + 2k_5\sum_{i=0}^{m-1}[BE_i][FF_{m-i-1}]\}\delta_{m0}$$

$$\frac{d[FF_m]}{dt} = -2k_3[FF_m][NaOH] + k_2[EP][BF_m] - 2k_5[FF_m]\{\sum_{n=0}^{\infty}\{[AB_n] + 2[BB_n] + 2[BE_n] + [BF_n]\} + \{k_4\sum_{i=0}^{m-1}[BF_i][EF_{m-i-1}] + 2k_5\sum_{i=0}^{m-1}[BF_i][FF_{m-i-1}]\}\delta_{m0}$$

$\delta_{m0} = 0$, for $m = 0$

$\delta_{m0} = 1$, for $m > 0$

Table 5

Moment Equations in a Batch Reactor

$$\frac{d\lambda^0_{AA}}{dt} = -2k_1[NaOH]\lambda^0_{AA} + k_4\lambda^0_{AB}\lambda^0_{AE} + k_5\lambda^0_{AB}\lambda^0_{AF}$$

$$\frac{d\lambda^0_{AB}}{dt} = -k_1[NaOH]\lambda^0_{AB} + 2k_1\lambda^0_{AA}[NaOH] - k_2\lambda^0_{AB}[EP] - k_4\lambda^0_{AB}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\} - k_5\lambda^0_{AB}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + 2k_4\lambda^0_{BB}\lambda^0_{AE} + 2k_5\lambda^0_{BB}\lambda^0_{AF}$$

$$\frac{d\lambda^0_{AE}}{dt} = -k_1[NaOH]\lambda^0_{AE} + k_3\lambda^0_{AF}[NaOH] - k_4\lambda^0_{AE}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\} + 2k_4\lambda^0_{AB}\lambda^0_{EE} + k_5\lambda^0_{BE}\lambda^0_{AF} + k_5\lambda^0_{AB}\lambda^0_{EF}$$

$$\frac{d\lambda^0_{AF}}{dt} = -k_1[NaOH]\lambda^0_{AF} + k_2\lambda^0_{AB}[EP] - k_3\lambda^0_{AF}[NaOH] - k_5\lambda^0_{AF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE}\} + k_4\lambda^0_{BF}\lambda^0_{AE} + k_4\lambda^0_{AB}\lambda^0_{EF} + 2k_5\lambda^0_{AB}\lambda^0_{FF}$$

$$\frac{d\lambda^0_{BB}}{dt} = k_1[NaOH]\lambda^0_{AB} - 2k_2\lambda^0_{BB}[EP] - 2k_4\lambda^0_{BB}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\} - 2k_5\lambda^0_{BB}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\}$$

$$\frac{d\lambda^0_{BE}}{dt} = k_1[NaOH]\lambda^0_{AE} - k_2\lambda^0_{BE}[EP] + k_3\lambda^0_{BF}[NaOH] - k_4\lambda^0_{BE}\{\lambda^0_{AE} + 2\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE} + \lambda^0_{BF} + 2\lambda^0_{EE} + \lambda^0_{EF}\} - k_5\lambda^0_{BE}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + 4k_4\lambda^0_{BB}\lambda^0_{EE} + 2k_5\lambda^0_{BB}\lambda^0_{EF}$$

$$\frac{d\lambda^0_{BF}}{dt} = k_1[NaOH]\lambda^0_{AF} + 2k_2\lambda^0_{BB}[EP] - k_2\lambda^0_{BF}[EP] - k_3\lambda^0_{BF}[NaOH] - k_4\lambda^0_{BF}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\} - k_5\lambda^0_{BF}\{\lambda^0_{AF} + \lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE} + \lambda^0_{BF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + 2k_4\lambda^0_{BB}\lambda^0_{EF} + 4k_5\lambda^0_{BB}\lambda^0_{FF}$$

$$\frac{d\lambda^0_{EE}}{dt} = k_3[NaOH]\lambda^0_{EF} - 2k_4\lambda^0_{EE}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\} + k_5\lambda^0_{BE}\lambda^0_{EF}$$

(Table 5 continued ... a)

Table 5 (continued ... a)

$$\frac{d\lambda^0_{EF}}{dt} = k_2[EP]\lambda^0_{BE} - k_3\lambda^0_{EF}[NaOH] + 2k_3\lambda^0_{FF}[NaOH] - k_4\lambda^0_{EF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\}$$
$$- k_5\lambda^0_{EF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE}\} + 2k_4\lambda^0_{BF}\lambda^0_{EE} + 2k_5\lambda^0_{BE}\lambda^0_{FF}$$

$$\frac{d\lambda^0_{FF}}{dt} = k_2[EP]\lambda^0_{BF} - 2k_3\lambda^0_{FF}[NaOH] - 2k_5\lambda^0_{FF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE}\} + k_4\lambda^0_{BF}\lambda^0_{EF}$$

$$\frac{d\lambda^1_{AA}}{dt} = -2k_1[NaOH]\lambda^1_{AA} + k_4\{\lambda^1_{AB}\lambda^0_{AE} + \lambda^0_{AB}\lambda^1_{AE}\} + k_5\{\lambda^1_{AB}\lambda^0_{AF} + \lambda^0_{AB}\lambda^1_{AF}\}$$

$$\frac{d\lambda^1_{AB}}{dt} = -k_1[NaOH]\lambda^1_{AB} + 2k_1\lambda^1_{AA}[NaOH] - k_2\lambda^1_{AB}[EP] - k_4\lambda^1_{AB}\{\lambda^0_{AE} + 2\lambda^0_{EE} +$$
$$\lambda^0_{EF}\} - k_5\lambda^1_{AB}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + 2k_4\{\lambda^1_{BB}\lambda^0_{AE} + \lambda^0_{BB}\lambda^1_{AE}\}$$
$$+ 2k_5\{\lambda^1_{BB}\lambda^0_{AF} + \lambda^0_{BB}\lambda^1_{AF}\} + k_4\lambda^0_{AB}\lambda^1_{BE} + k_5\lambda^0_{AB}\lambda^1_{BF}$$

$$\frac{d\lambda^1_{AE}}{dt} = -k_1[NaOH]\lambda^1_{AE} + k_3\lambda^1_{AF}[NaOH] - k_4\lambda^1_{AE}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\} + k_4\lambda^1_{BE}\lambda^0_{AE}$$
$$+ 2k_4\{\lambda^1_{AB}\lambda^0_{EE} + \lambda^0_{AB}\lambda^1_{EE}\} + k_5\{\lambda^1_{BE}\lambda^0_{AF} + \lambda^0_{BE}\lambda^1_{AF}\} + k_5\{\lambda^1_{AB}\lambda^0_{EF} + \lambda^0_{AB}\lambda^1_{EF}\}$$

$$\frac{d\lambda^1_{AF}}{dt} = -k_1[NaOH]\lambda^1_{AF} + k_2\lambda^1_{AB}[EP] - k_3\lambda^1_{AF}[NaOH] - k_5\lambda^1_{AF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE}\}$$
$$+ k_4\{\lambda^1_{BF}\lambda^0_{AE} + \lambda^0_{BF}\lambda^1_{AE}\} + k_4\{\lambda^1_{AB}\lambda^0_{EF} + \lambda^0_{AB}\lambda^1_{EF}\} + k_5\lambda^1_{BF}\lambda^0_{AF}$$
$$+ 2k_5\{\lambda^1_{AB}\lambda^0_{FF} + \lambda^0_{AB}\lambda^1_{FF}\}$$

$$\frac{d\lambda^1_{BB}}{dt} = k_1[NaOH]\lambda^1_{AB} - 2k_2\lambda^1_{BB}[EP] - 2k_4\lambda^1_{BB}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\} - 2k_5\lambda^1_{BB}\{\lambda^0_{AF} + \lambda^0_{EF}$$
$$+ 2\lambda^0_{FF}\} + 2k_4\lambda^0_{BB}\lambda^1_{BE} + 2k_5\lambda^0_{BB}\lambda^1_{BF}$$

$$\frac{d\lambda^1_{BE}}{dt} = k_1[NaOH]\lambda^1_{AE} - k_2\lambda^1_{BE}[EP] + k_3\lambda^1_{BF}[NaOH] - k_4\lambda^1_{BE}\{\lambda^0_{AE} + \lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE} + \lambda^0_{BF}$$
$$+ 2\lambda^0_{EE} + \lambda^0_{EF}\} - k_5\lambda^1_{BE}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + k_4\lambda^0_{BE}\lambda^1_{BE} + 4k_4\{\lambda^1_{BB}\lambda^0_{EE} + \lambda^0_{BB}\lambda^1_{EE}\}$$
$$+ k_5\lambda^0_{BE}\lambda^1_{BF} + 2k_5\{\lambda^1_{BB}\lambda^0_{EF} + \lambda^0_{BB}\lambda^1_{EF}\}$$

$$\frac{d\lambda^1_{BF}}{dt} = k_1[NaOH]\lambda^1_{AF} + 2k_2\lambda^1_{BB}[EP] - k_2\lambda^1_{BF}[EP] - k_3\lambda^1_{BF}[NaOH] - k_4\lambda^1_{BF}\{\lambda^0_{AE} + 2\lambda^0_{EE}$$
$$+ \lambda^0_{EF}\} - k_5\lambda^1_{BF}\{\lambda^0_{AF} + \lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE} + \lambda^0_{BF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + k_4\lambda^0_{BF}\lambda^1_{BE}$$
$$+ 2k_4\{\lambda^1_{BB}\lambda^0_{EF} + \lambda^0_{BB}\lambda^1_{EF}\} + k_5\lambda^0_{BF}\lambda^1_{BF} + 4k_5\{\lambda^1_{BB}\lambda^0_{FF} + \lambda^0_{BB}\lambda^1_{FF}\}$$

(Table 5 continued ... b)

Table 5 (Continued ... b)

$$\frac{d\lambda^1_{EE}}{dt} = k_3[NaOH]\lambda^1_{EF} - 2k_4\lambda^1_{EE}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\} + 2k_4\lambda^1_{BE}\lambda^0_{EE} + k_5\{\lambda^1_{BE}\lambda^0_{EF} + \lambda^0_{BE}\lambda^1_{EF}\}$$

$$\frac{d\lambda^1_{EF}}{dt} = k_2[EP]\lambda^1_{BE} - k_3\lambda^1_{EF}[NaOH] + 2k_3\lambda^1_{FF}[NaOH] - k_4\lambda^1_{EF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\} - k_5\lambda^1_{EF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + 2\lambda^0_{BE}\} + 2k_4\{\lambda^1_{BF}\lambda^0_{EE} + \lambda^0_{BF}\lambda^1_{EE}\} + k_4\lambda^1_{BE}\lambda^0_{EF} + k_5\lambda^1_{BF}\lambda^0_{EF} + 2k_5\{\lambda^1_{BE}\lambda^0_{FF} + \lambda^0_{BE}\lambda^1_{FF}\}$$

$$\frac{d\lambda^1_{FF}}{dt} = k_2[EP]\lambda^1_{BF} - 2k_3\lambda^1_{FF}[NaOH] - 2k_5\lambda^1_{FF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE}\} + k_4\{\lambda^1_{BF}\lambda^0_{EF} + \lambda^0_{BF}\lambda^1_{EF}\} + 2k_5\lambda^1_{BF}\lambda^0_{FF}$$

$$\frac{d\lambda^2_{AA}}{dt} = -2k_1[NaOH]\lambda^2_{AA} + k_4\{\lambda^2_{AB}\lambda^0_{AE} + \lambda^0_{AB}\lambda^2_{AE} + 2\lambda^1_{AB}\lambda^1_{AE}\} + k_5\{\lambda^2_{AB}\lambda^0_{AF} + \lambda^0_{AB}\lambda^2_{AF} + 2\lambda^1_{AB}\lambda^1_{AF}\}$$

$$\frac{d\lambda^2_{AB}}{dt} = -k_1[NaOH]\lambda^2_{AB} + 2k_1\lambda^1_{AA}[NaOH] - k_2\lambda^2_{AB}[EP] - k_4\lambda^2_{AB}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\} - k_5\lambda^2_{AB}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + 2k_4\{\lambda^2_{BB}\lambda^0_{AE} + \lambda^0_{BB}\lambda^2_{AE} + 2\lambda^1_{BB}\lambda^1_{AE}\} + 2k_5\{\lambda^2_{BB}\lambda^0_{AF} + \lambda^0_{BB}\lambda^2_{AF} + 2\lambda^1_{BB}\lambda^1_{AF}\} + k_4\{\lambda^0_{AB}\lambda^2_{BE} + 2\lambda^1_{AB}\lambda^1_{BE}\} + k_5\{\lambda^0_{AB}\lambda^2_{BF} + 2\lambda^1_{AB}\lambda^1_{BF}\}$$

$$\frac{d\lambda^2_{AE}}{dt} = -k_1\lambda^2_{AE}[NaOH] + k_3\lambda^2_{AF}[NaOH] - k_4\lambda^2_{AE}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\} + k_4\{\lambda^2_{BE}\lambda^0_{AE} + 2\lambda^1_{BE}\lambda^1_{AE}\} + 2k_4\{\lambda^2_{AB}\lambda^0_{EE} + \lambda^0_{AB}\lambda^2_{EE} + 2\lambda^1_{AB}\lambda^1_{EE}\} + k_5\{\lambda^2_{BE}\lambda^0_{AF} + \lambda^0_{BE}\lambda^2_{AF} + 2\lambda^1_{BE}\lambda^1_{AF}\} + k_5\{\lambda^2_{AB}\lambda^0_{EF} + \lambda^0_{AB}\lambda^2_{EF} + 2\lambda^1_{AB}\lambda^1_{EF}\}$$

$$\frac{d\lambda^2_{AF}}{dt} = -k_1[NaOH]\lambda^2_{AF} + k_2\lambda^2_{AB}[EP] - k_3\lambda^2_{AF}[NaOH] - k_5\lambda^2_{AF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE}\} + k_4\{\lambda^2_{BF}\lambda^0_{AE} + \lambda^0_{BF}\lambda^2_{AE} + 2\lambda^1_{BF}\lambda^1_{AE}\} + k_4\{\lambda^2_{AB}\lambda^0_{EF} + \lambda^0_{AB}\lambda^2_{EF} + 2\lambda^1_{AB}\lambda^1_{EF}\} + k_5\{\lambda^2_{BF}\lambda^0_{AF} + 2\lambda^1_{BF}\lambda^1_{AF}\} + 2k_5\{\lambda^2_{AB}\lambda^0_{FF} + \lambda^0_{AB}\lambda^2_{FF} + 2\lambda^1_{AB}\lambda^1_{FF}\}$$

$$\frac{d\lambda^2_{BB}}{dt} = k_1[NaOH]\lambda^2_{AB} - 2k_2\lambda^2_{BB}[EP] - 2k_4\lambda^2_{BB}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\} - 2k_5\lambda^2_{BB}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + 2k_4\{\lambda^0_{BB}\lambda^2_{BE} + 2\lambda^1_{BB}\lambda^1_{BE}\} + 2k_5\{\lambda^0_{BB}\lambda^2_{BF} + 2\lambda^1_{BB}\lambda^1_{BF}\}$$

(Table 5 continued ...c)

Table 5 (Continued ... c)

$$\frac{d\lambda^2_{BE}}{dt} = k_1[NaOH]\lambda^2_{AE} - k_2\lambda^2_{BE}[EP] + k_3\lambda^2_{BF}[NaOH] - k_4\lambda^2_{BE}\{\lambda^0_{AE} + \lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE} + \lambda^0_{BF} + 2\lambda^0_{EE} + \lambda^0_{EF}\} - k_5\lambda^2_{BE}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + k_4\{\lambda^0_{BE}\lambda^2_{BE} + 2\lambda^1_{BE}\lambda^1_{BE}\} + 4k_4\{\lambda^2_{BB}\lambda^0_{EE} + \lambda^0_{BB}\lambda^2_{EE} + 2\lambda^1_{BB}\lambda^1_{EE}\} + k_5\{\lambda^0_{BE}\lambda^2_{BF} + 2\lambda^1_{BE}\lambda^1_{BF}\} + 2k_5\{\lambda^2_{BB}\lambda^0_{EF} + \lambda^0_{BB}\lambda^2_{EF} + 2\lambda^1_{BB}\lambda^1_{EF}\}$$

$$\frac{d\lambda^2_{BF}}{dt} = k_1[NaOH]\lambda^2_{AF} + 2k_2\lambda^2_{BB}[EP] - k_2\lambda^2_{BF}[EP] - k_3\lambda^2_{BF}[NaOH] - k_4\lambda^2_{BF}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\} - k_5\lambda^2_{BF}\{\lambda^0_{AF} + \lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE} + \lambda^0_{BF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + k_4\{\lambda^0_{BF}\lambda^2_{BE} + 2\lambda^1_{BF}\lambda^1_{BE}\} + 2k_4\{\lambda^2_{BB}\lambda^0_{EF} + \lambda^0_{BB}\lambda^2_{EF} + 2\lambda^1_{BB}\lambda^1_{EF}\} + k_5\{\lambda^0_{BF}\lambda^2_{BF} + 2\lambda^1_{BF}\lambda^1_{BF}\} + 4k_5\{\lambda^2_{BB}\lambda^0_{FF} + \lambda^0_{BB}\lambda^2_{FF} + 2\lambda^1_{BB}\lambda^1_{FF}\}$$

$$\frac{d\lambda^2_{EE}}{dt} = k_3[NaOH]\lambda^2_{EF} - 2k_4\lambda^2_{EE}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\} + 2k_4\{\lambda^2_{BE}\lambda^0_{EE} + 2\lambda^1_{BE}\lambda^1_{EE}\} + k_5\{\lambda^2_{BE}\lambda^0_{EF} + \lambda^0_{BE}\lambda^2_{EF} + 2\lambda^1_{BE}\lambda^1_{EF}\}$$

$$\frac{d\lambda^2_{EF}}{dt} = k_2[EP]\lambda^2_{BE} - k_3\lambda^2_{EF}[NaOH] + 2k_3\lambda^2_{FF}[NaOH] - k_4\lambda^2_{EF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\} - k_5\lambda^2_{EF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + 2\lambda^0_{BE}\} + 2k_4\{\lambda^2_{BF}\lambda^0_{EE} + \lambda^0_{BF}\lambda^2_{EE} + 2\lambda^1_{BF}\lambda^1_{EE}\} + k_4\{\lambda^2_{BE}\lambda^0_{EF} + 2\lambda^1_{BE}\lambda^1_{EF}\} + k_5\{\lambda^2_{BF}\lambda^0_{EF} + 2\lambda^1_{BF}\lambda^1_{EF}\} + 2k_5\{\lambda^2_{BE}\lambda^0_{FF} + \lambda^0_{BE}\lambda^2_{FF} + 2\lambda^1_{BE}\lambda^1_{FF}\}$$

$$\frac{d\lambda^2_{FF}}{dt} = k_2[EP]\lambda^2_{BF} - 2k_3\lambda^2_{FF}[NaOH] - 2k_5\lambda^2_{FF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE}\} + k_4\{\lambda^2_{BF}\lambda^0_{EF} + \lambda^0_{BF}\lambda^2_{EF} + 2\lambda^1_{BF}\lambda^1_{EF}\} + 2k_5\{\lambda^2_{BF}\lambda^0_{FF} + 2\lambda^1_{BF}\lambda^1_{FF}\}$$

Table 6

Concentration of Various End Groups

$$[A] = \sum_{n=0}^{\infty}(2[AA_n] + [AB_n] + [AE_n] + [AF_n])$$

$$[B] = \sum_{n=0}^{\infty}(2[BB_n] + [AB_n] + [BE_n] + [BF_n])$$

$$[E] = \sum_{n=0}^{\infty}(2[EE_n] + [AE_n] + [BE_n] + [BF_n])$$

$$[F] = \sum_{n=0}^{\infty}(2[FF_n] + [AF_n] + [BF_n] + [EF_n])$$

available) can be written using the simplified kinetic scheme (in terms of end groups) of Table 1. These are given in Table 7. The following checks were made to confirm the correctness of the balance equations.

(a) It was found that the equations obtained by appropriately summing up the equations in Table 4 (using Table 6), were identical to the balance equations for the end groups (given in Table 7 and derived independently using the simplified kinetic scheme of Table 1). The same check was made using the equations for the zeroth moments (Table 5) and the equations matched with those in Table 7. This confirmed the correctness of the equations for the zeroth moment, as well as partially confirmed the correctness of the mole balance equations in Table 4.

(b) In a batch reactor, the total moles of the aryl unit, R, is conserved, i.e., the moles of R at any time (distributed over the several molecular species given in Table 2) must be equal to the moles of R initially (in bisphenol A). This has been checked out, and confirms that the equations are correct.

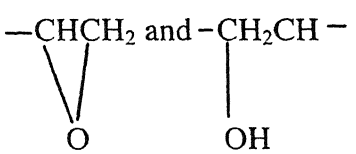
(c) In a batch reactor, the sum of the moles of the two groups,  should be constant with time and should be equal to the initial moles of epichlorohydrin present. An equation for the total number of the above repeat units (distributed over the several molecular species in Table 2) was written (in terms of the moments). It was found that this check was also satisfied.

Table 7

Mole Balance Equations for the End Groups and Some Lower Oligomers in a Batch Reactor

$$\frac{d[A]}{dt} = -k_1[NaOH][A]$$

$$\frac{d[B]}{dt} = k_1[NaOH][A] - k_2[EP][B] - k_4[E][B] - k_5[F][B]$$

$$\frac{d[E]}{dt} = k_3[NaOH][F] - k_4[B][E]$$

$$\frac{d[F]}{dt} = k_2[EP][B] - k_3[NaOH][F] - k_5[B][F]$$

$$\frac{d[EP]}{dt} = -k_2[EP][B]$$

$$\frac{d[NaOH]}{dt} = -k_1[NaOH][A] + k_2[EP][B] - k_3[NaOH][F] + k_4[B][E] = -\frac{d[H_2O]}{dt}$$

$$\frac{d[NaCl]}{dt} = k_3[NaOH][F] + k_5[B][F]$$

$$\frac{d[AA_0]}{dt} = -2k_1[NaOH][AA_0]$$

$$\frac{d[AE_0]}{dt} = -k_1[NaOH][AE_0] + k_3[AF_0][NaOH] - k_4[AE_0][B]$$

(Table 7 Continued ... a)

Table 7 (continued ... a)

$$\frac{d[AF_0]}{dt} = -k_1[NaOH][AF_0] + k_2[AB_0][EP] - k_3[AF_0][NaOH] - k_5[AF_0][B]$$

$$\frac{d[FF_0]}{dt} = k_2[EP][BF_0] - 2k_3[FF_0][NaOH] - 2k_5[FF_0][B]$$

$$\frac{d[EE_0]}{dt} = k_3[NaOH][EF_0] - 2k_4[EE_0][B]$$

$$\frac{d[AB_0]}{dt} = -k_1[NaOH]\{[AB_0] - 2[AA_0]\} - k_2[AB_0][EP] - k_4[AB_0][E] - k_5[AB_0][F]$$

$$\frac{d[BE_0]}{dt} = k_1[NaOH][AE_0] - k_2[BE_0][EP] + k_3[BF_0][NaOH] - k_4[BE_0]\{[B] + [E]\} - k_5[BE_0][F]$$

$$\frac{d[BB_0]}{dt} = k_1[NaOH][AB_0] - 2k_2[BB_0][EP] - 2k_4[BB_0][E] - 2k_5[BB_0][F]$$

$$\frac{d[BF_0]}{dt} = k_1[NaOH][AF_0] + 2k_2[BB_0][EP] - k_2[BF_0][EP] - k_3[BF_0][NaOH] - k_4[BF_0]\{[B] + [E]\} - k_5[BF_0][F]$$

$$\frac{d[EF_0]}{dt} = k_1[EP][BE_0] - k_3[EF_0][NaOH] + 2k_3[FF_0][NaOH] - k_4[EF_0][B] - k_5[EF_0][B]$$

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The above three checks were sufficient to confirm the correctness of the mole and moment balance equations in Tables 4 and 5.

The equations in Table 5 (alongwith those for [NaOH] and [EP] from Table 7) form a complete set of ODEs (initial value problem-IVP), which can be integrated for any given set of initial conditions for a specified temperature history and specified rate constants (k_1-k_5). Similarly, the equations in Table 7 form another complete set of ODE-IVPs and can be integrated separately. The numerical technique used to integrate these equations is Gear's algorithm.[12] The NAG library routine, D02EBF, which has a built-in step size control algorithm and is particularly useful for stiff systems, is used (with a tolerance, TOL, of 10^{-7}) for this purpose. Changing the value of the parameter, TOL, led to almost identical results. The three checks described above were also made with the computer code to ensure the correctness of the simulation program.

With the mathematical model and computer code now developed, we can start obtaining some useful results. Some experimental data on isothermal (25° C) polymerization of bisphenol A with epichlorohydrin with NaOH catalyst (in cellosolve solvent) has been provided by Batzer and Zahir.[1] These could be used to obtain curve-fit values for the five rate constants at 25° C. Similarly, curve fitting can be attempted at other temperatures when additional experimental data becomes available to give Arrhenius expressions for the rate constants (unfortunately, experimental work along the lines required are not available in the open literature). The Box complex procedure[13,14] is used to carry out the curve-fitting exercise for the data presented by Batzer and Zahir.[1] This technique minimizes an objective function, E, using a pattern-search technique. The

objective function is chosen as a weighted sum of absolute errors between the values predicted by the model and experimental data. It is given by

$$E(k_1,k_2,k_3,k_4,k_5) = \sum_j W_j \frac{1}{N_{j,exp}} \sum_i \left| \frac{[j]_{i,theor} - [j]_{i,exp}}{[j]_{i,exp}} \right| \quad (3)$$

In the above equation, [j] is the concentration of the jth molecular species for which experimental data is available,[1] W_j is the weightage factor assigned to the experimental data set for the jth oligomer (or summation of oligomers), and subscript i indicates the ith data point in a set for the jth species. Superscripts, exp and theor, represent experimental and the corresponding theoretical values for any concentration. $N_{j,exp}$ indicates the number of experimental data points available for the jth species. Minimization of E while searching for values of k_1-k_5 leads to a nonlinear best-fit set of values for these rate constants. The CPU time taken on a mainframe HP9000/850 S supermini computer for the parameter estimation (220 iterations) is 28.64 s.

Chapter 3

Results and Discussion

The Box complex algorithm is used with the experimental data of Batzer and Zahir[1] to obtain the best-fit values of the five parameters, k_1, k_2, k_3, k_4 and k_5, at 25^0 C. The initial conditions used are : $[AA_0]_0$=200 mol/m^3, $[EP]_0$=1280 mol/m^3, $[NaOH]_0$=400 mol/m^3. The parameters used in this program are given in Table 8. The experimental data[1] used in our study are the concentrations, $[AA_0]$ (bisphenol A), $[EE_0]$, $[EF_0]$, $[FF_0]$ and ($[AE_0]$+$[AF_0]$), at different times. The actual data of Batzer and Zahir (representing uncorrected peak heights of chromatographic curves) were nondimensionalised using the corresponding maximum values, while the chromatographic peak data on $[AA_0]$ was transformed into concentrations using the given initial concentration, $[AA_0]_0$. The optimal values of the rate constants are given in Table 8.

Fig. 1 shows how E varies with iteration number. It is observed that E slowly reaches its lowest value. Figs. 2, 3 and 1 show how significant changes occur in the values of k_1-k_5 before they also settle down to their best-fit values.

The best-fit values of the rate constants are used to generate the concentration histories of several lower oligomers. Figs. 4 - 6 show the quality of the curve-fit of the experimental data. These fits are observed to be fairly good. Figs. 7 and 8 show the variations of [EP], [NaOH], [NaCl] and [H_2O] with time, computed using the best-fit values of the rate constants. It is observed that reasonable amounts of NaOH are consumed leading to the production of water. The epichlorohydrin concentration does not

Table 8

Data Used and Results Obtained in Optimal Parameter Estimation

Weightage Factors Used in Eq. 3

Data Used	W_j
$[AA_0]$	1.0
$[EE_0]/[EE_0]_{max}$	1.0
$[EF_0]/[EF_0]_{max}$	1.0
$[FF_0]/[FF_0]_{max}$	5.0
$([AE_0]+[AF_0])/([AE_0]+[AF_0])_{max}$	1.0

Values of the Parameters Used in Box Complex Optimization

N=7

$\alpha = 1.3$

$\beta = 10^{-6}$

$\gamma = 3$

$\delta = 0.01(h_j - l_j)$ where, h_j and l_j are the upper and lower bounds on the jth parameter

Initial Value of the Parameters

$$[k_1, k_2, k_3, k_4, k_5] = [1.2\times10^{-3}, 3.1\times10^{-5}, 2.0\times10^{-4}, 6.4\times10^{-6}, 2.7\times10^{1}]$$

Bounds on the Parameters

$$5.0\times10^{-4} \le k_1 \le 1.5\times10^{-3}$$

$$1.0\times10^{-5} \le k_2 \le 9.0\times10^{-5}$$

$$1.0\times10^{-4} \le k_3 \le 9.0\times10^{-4}$$

$$1.0\times10^{-6} \le k_4 \le 9.0\times10^{-6}$$

$$1.0\times10^{1} \le k_5 \le 9.0\times10^{1}$$

Optimized Values of the Parameters

$$\begin{bmatrix} k_1 \\ k_2 \\ k_3 \\ k_4 \\ k_5 \end{bmatrix} = \begin{bmatrix} 1.011378\times10^{-3} \\ 6.316743\times10^{-5} \\ 3.949022\times10^{-4} \\ 2.2321728\times10^{-6} \\ 3.3116070\times10^{1} \end{bmatrix}$$

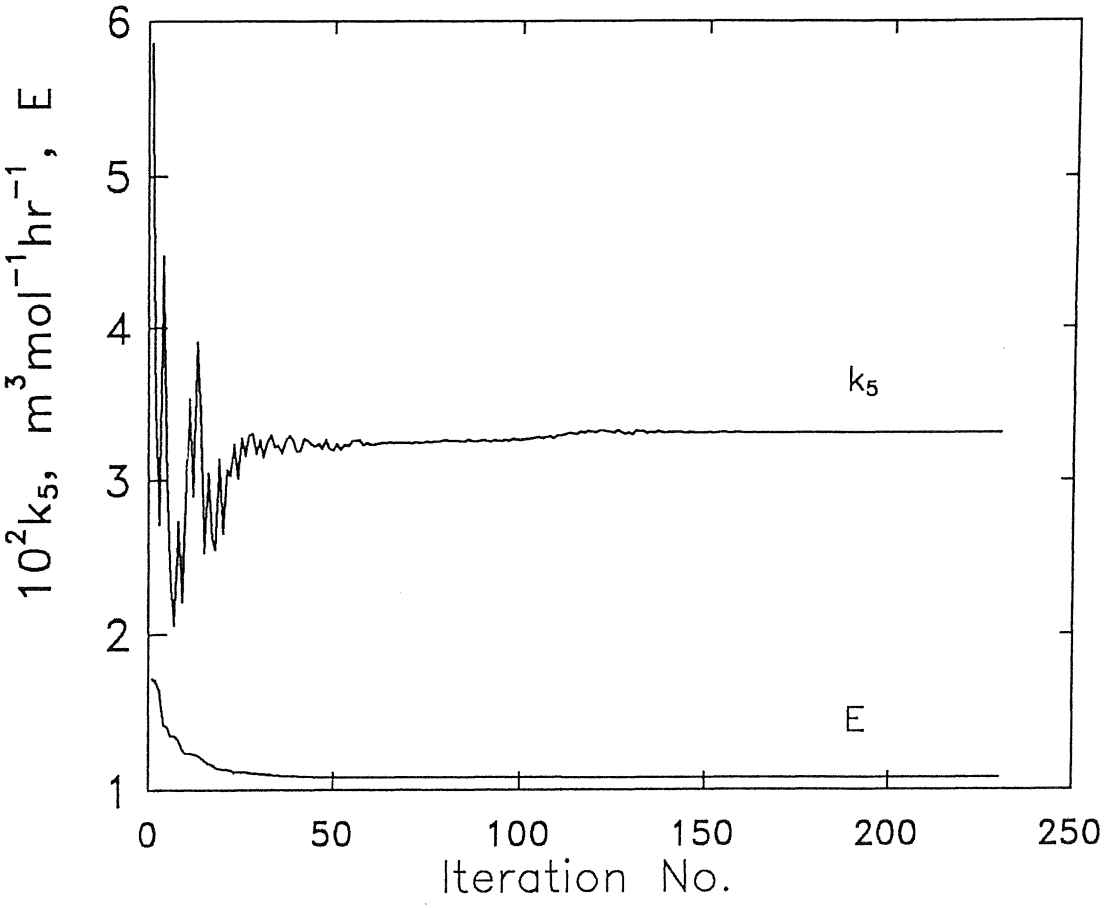

Fig. 1 : Variation of error and k_5 with iteration number.

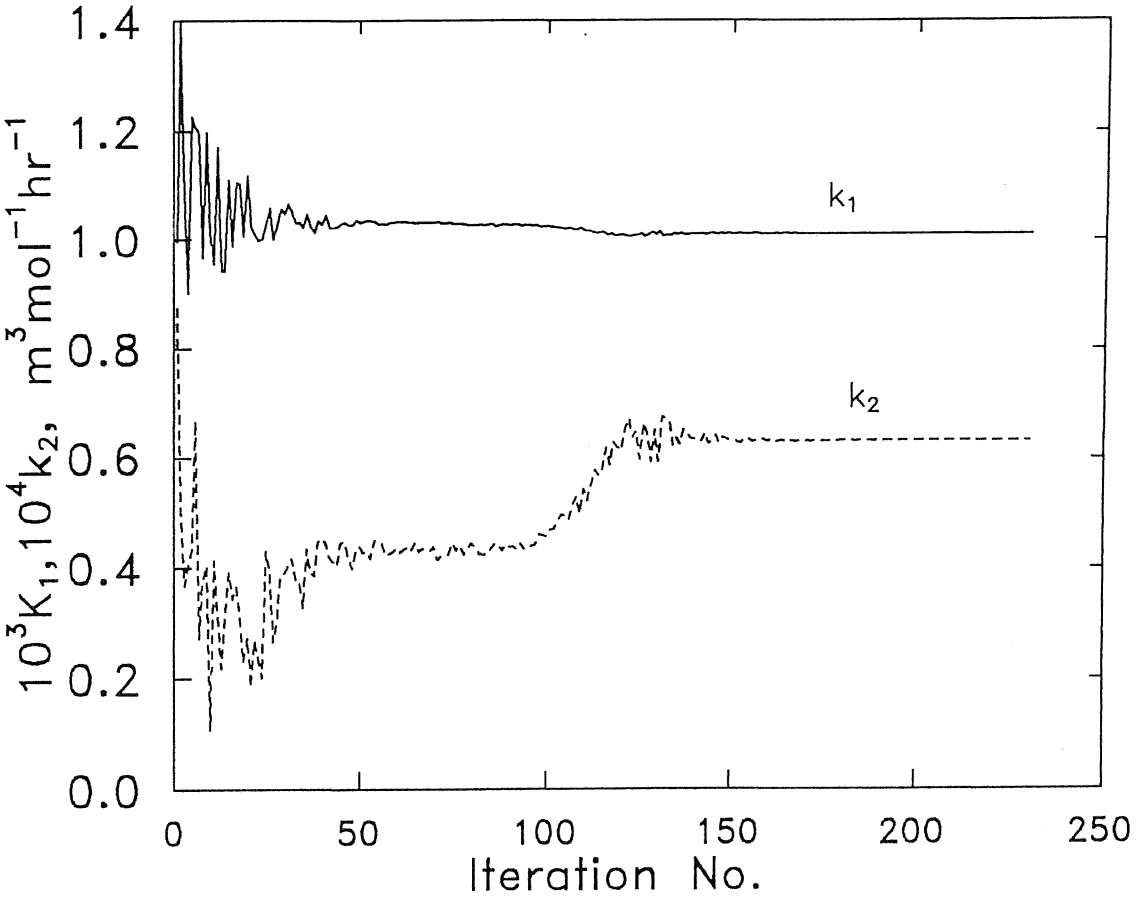

Fig. 2 : Variation of k_1 and k_2 with iteration number.

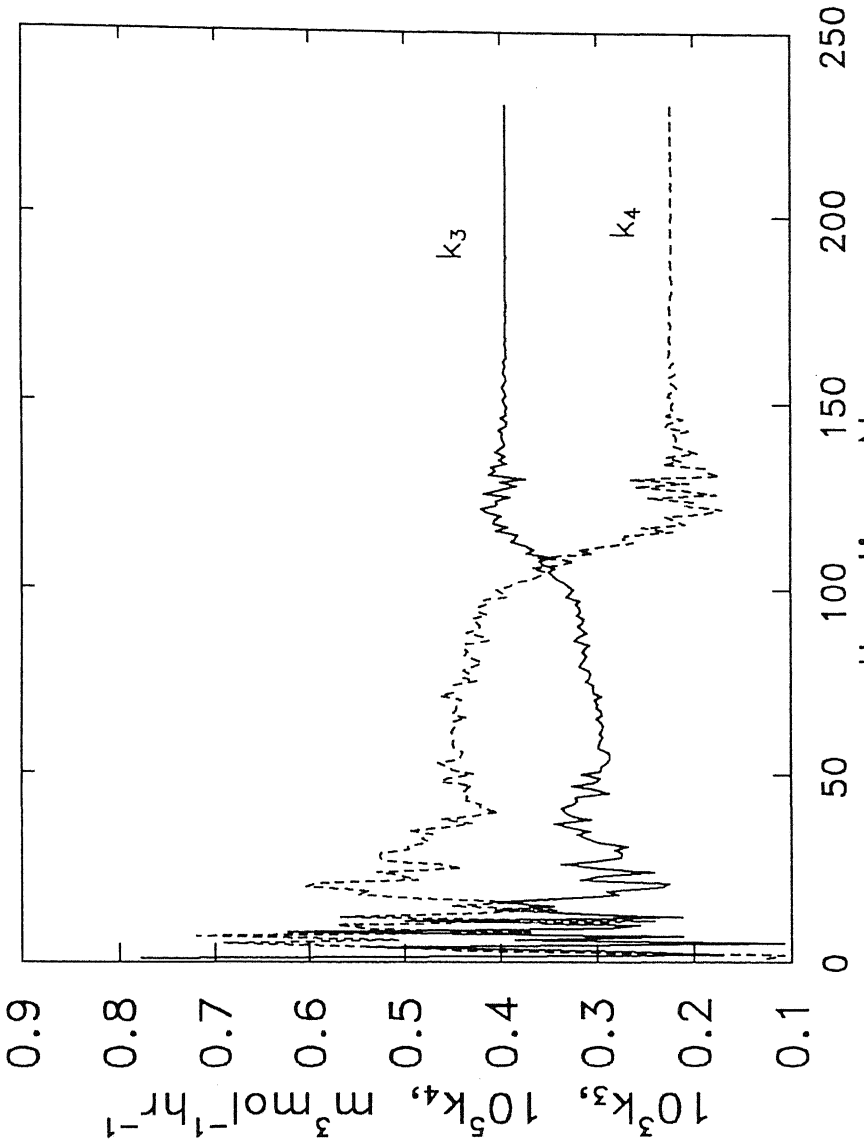

Fig. 3 : Variation of k_3 and k_4 with iteration number.

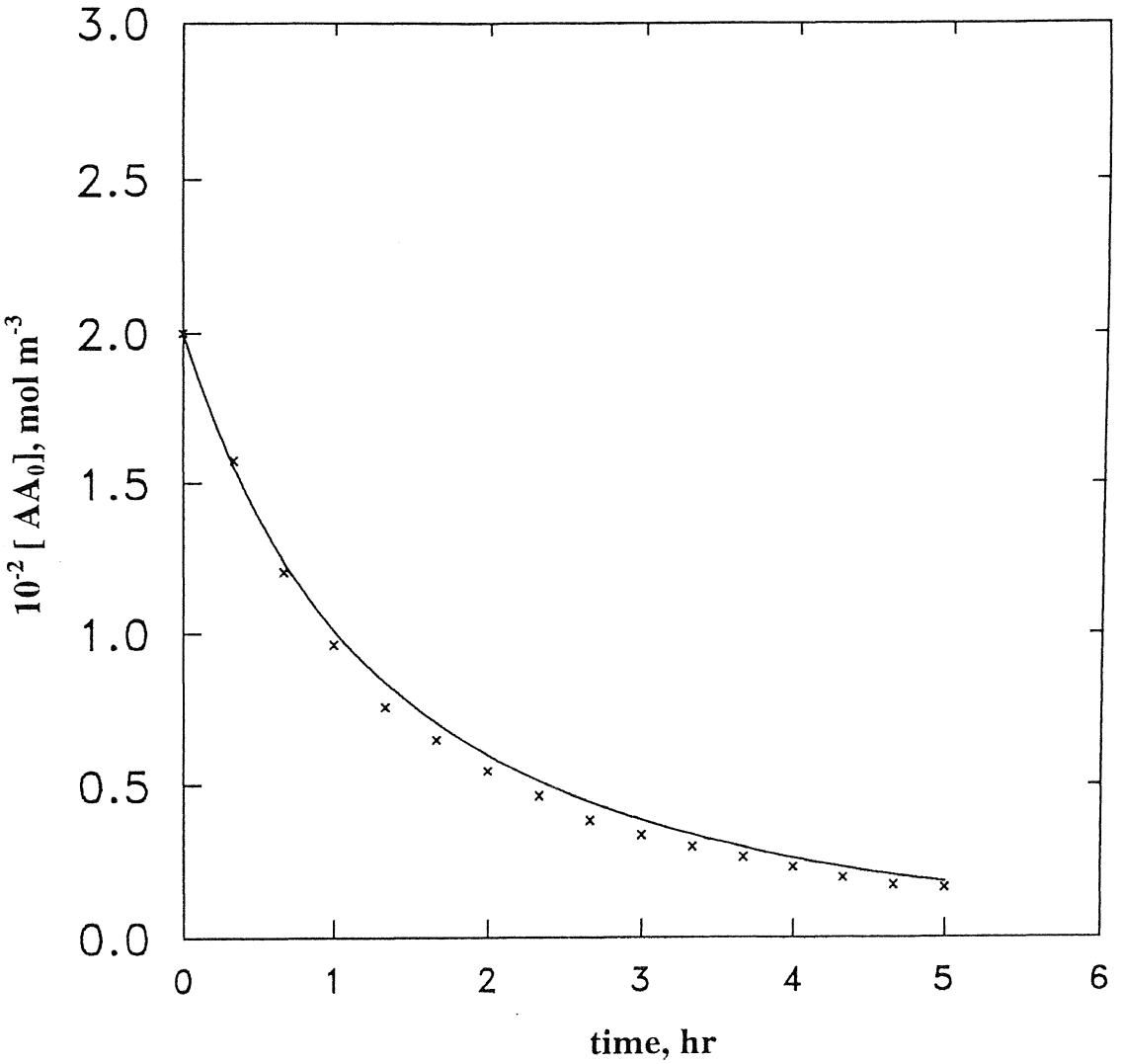

Fig. 4 : Variation of the concentration of bisphenol A with time. Experimental data of Batzer and Zahir[1] also shown. Curve indicates model predictions using the optimal parameters.

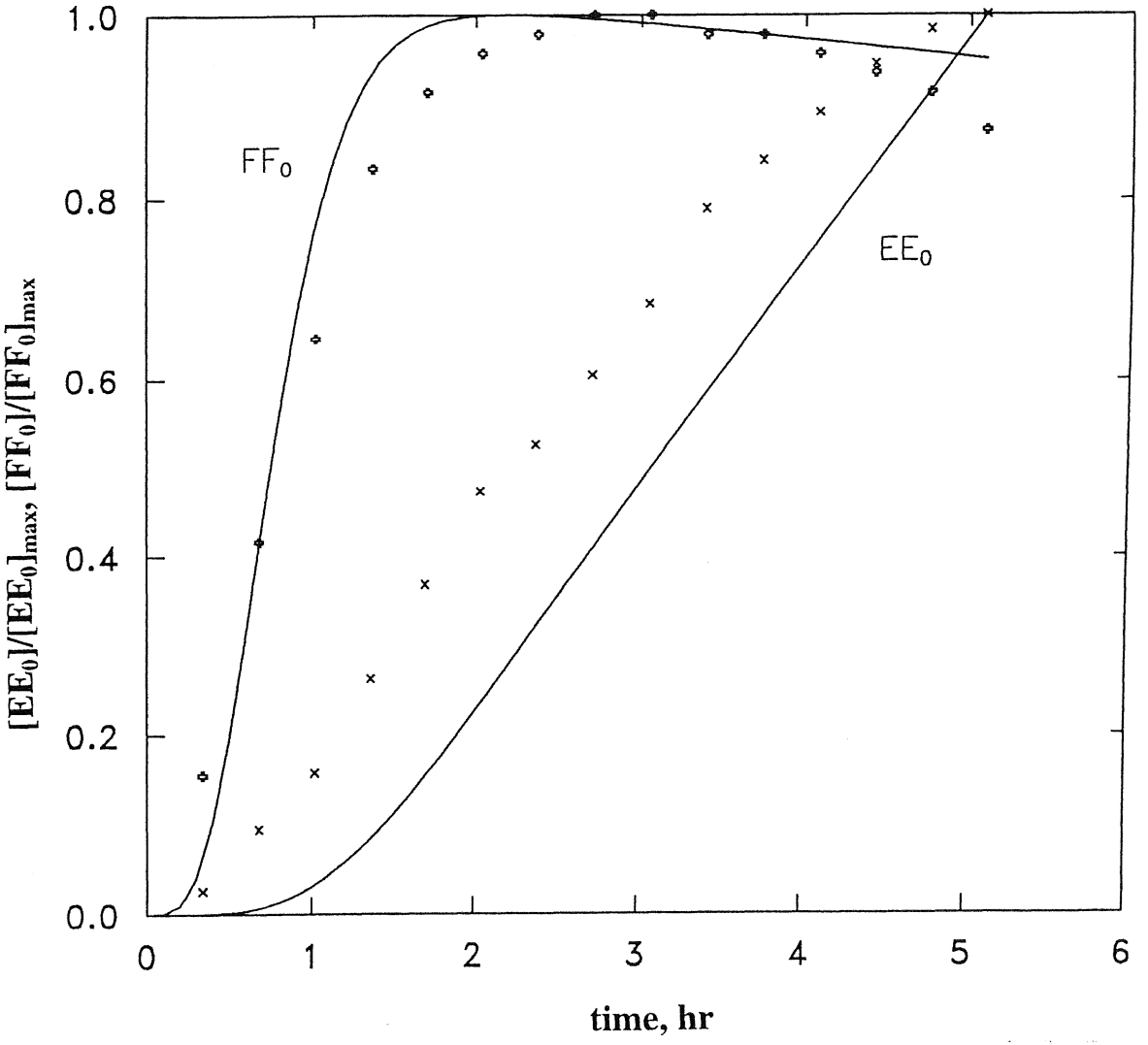

Fig. 5 : Variation of the dimensionless concentrations of EE_0 and FF_0 with time. Solid lines represent model predictions using optimal parameters. Symbols represent experimental data points of Batzer and Zahir[1].

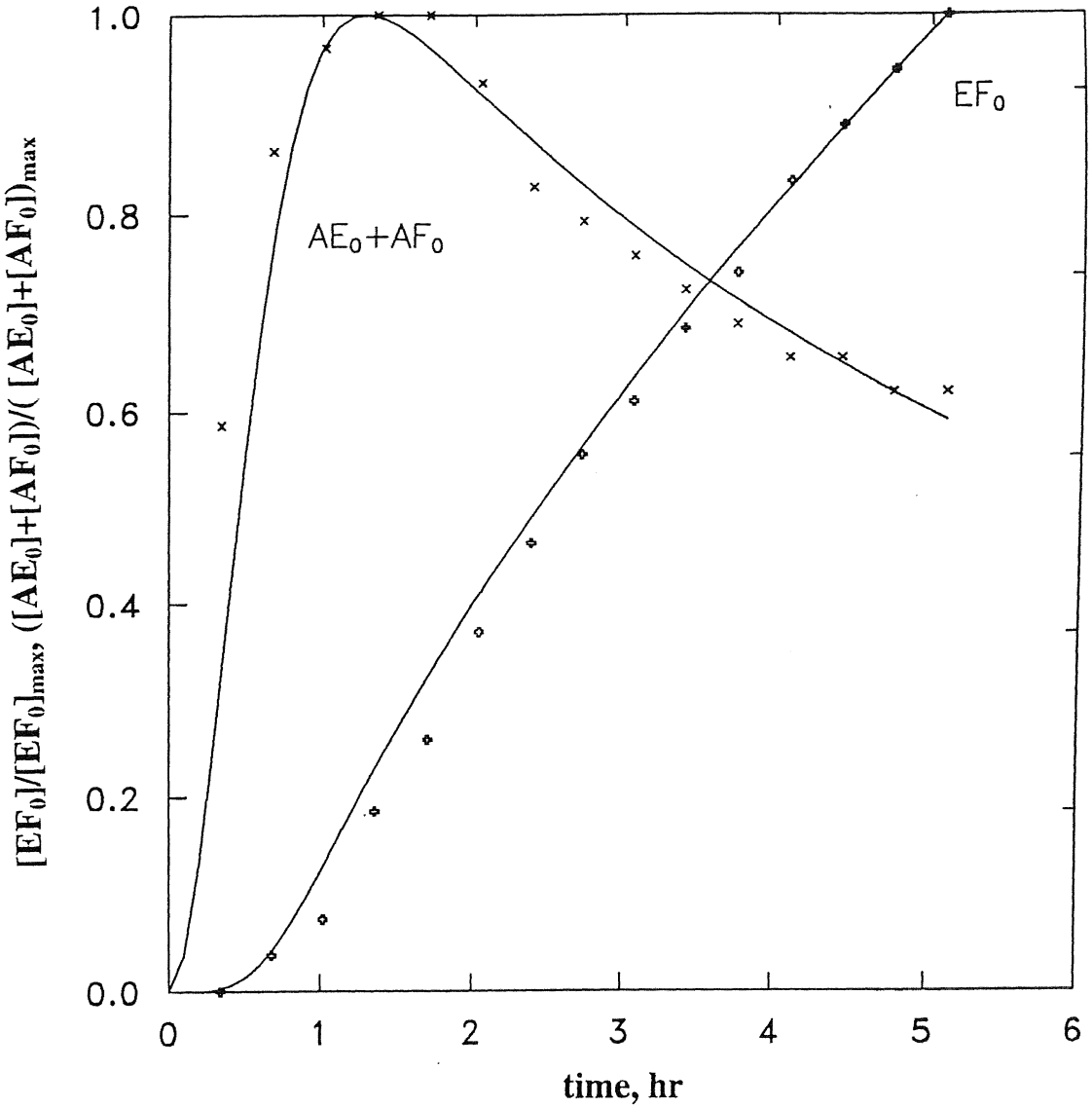

Fig. 6 : Variation of the dimensionless concentrations of AE_0+AF_0 and EF_0 with time. Solid lines represent model predictions using optimal parameters. Symbols represent the experimental data points of Batzer and Zahir[1].

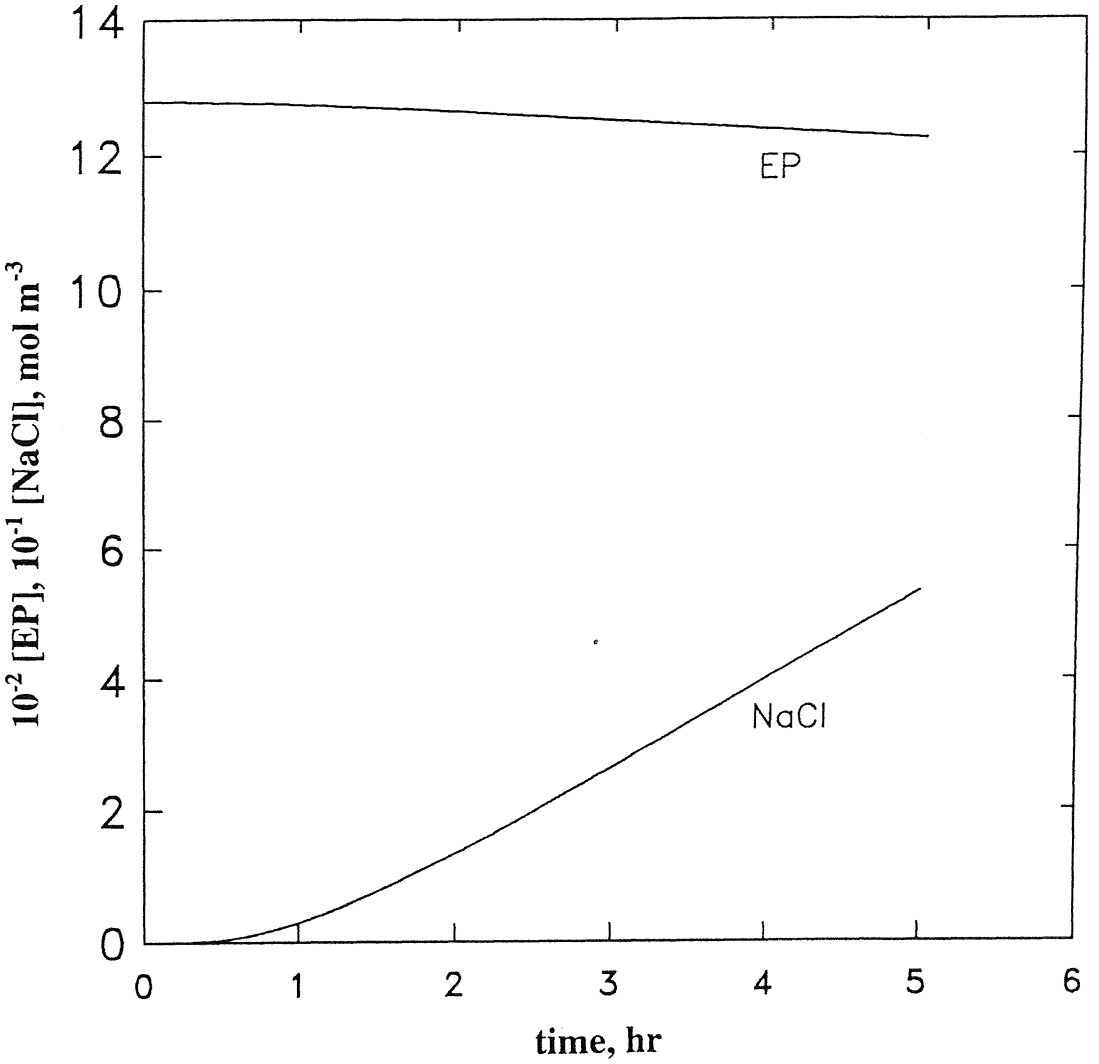

Fig. 7 : Variation of [EP] and [NaCl] with time. Optimal values of the rate constants used.

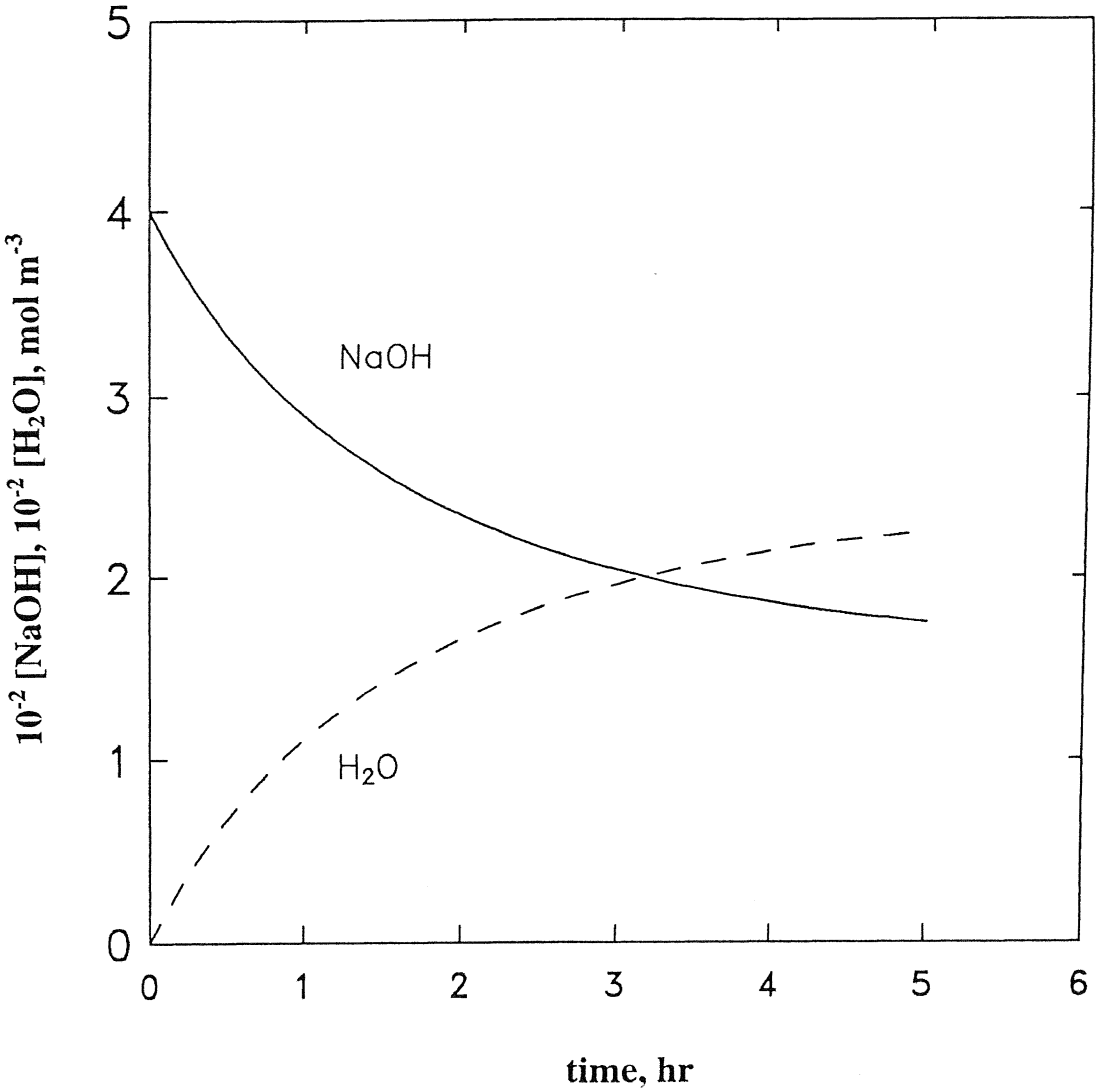

Fig. 8 : Variation of [NaOH] and [H_2O] with time. Optimal values of the rate constants used.

change much with time since it is taken in excess. Small amounts of NaCl are produced during the polymerization. This needs to be removed by washing with water at the end.

The optimized model parameters are used in the moment equations of Table 5 with $[AA_0]_0$=200 mol/m^3, $[EP]_0$=1280 mol/m^3 and $[NaOH]_0$=400 mol/m^3, to generate the number and weight average molecular weights, as well as the polydispersity index (with the help of Table 3). Fig. 9 shows the variation with time of the average molecular weights with and without the concentration of epichlorohydrin used in the computations. The value of M_n (without EP) is slightly over 342, the molecular weight of DGEBPA, near the end, and indicates that the end-capping of bisphenol A by excess epichlorohydrin is essentially complete. The PDI without EP rises from 1.0 to about 1.4 during this period. The PDI of about 1.4 at the end suggests that significant amounts of higher oligomers are also formed in this process.

Detailed sensitivity tests are now performed to identify the most important parameters, so that greater care can be taken in estimating their values. Fig. 10 shows that the bisphenol A concentration is somewhat sensitive to changes in the value of k_1. The other rate constants do not influence the concentration history of $[AA]_0$ as much. Similar sensitivities are observed for the concentration of NaOH. The concentration of NaCl, in contrast, is sensitive to variations in both k_1 and k_2, but not as sensitive to other rate constants. The epichlorohydrin concentration is not influenced much by any of the rate constants, since it is in large excess. The value of M_n (without EP) is most sensitive to variations in k_1 and k_2. Fig. 11 shows how higher values of M_n are attained when k_1 or k_2

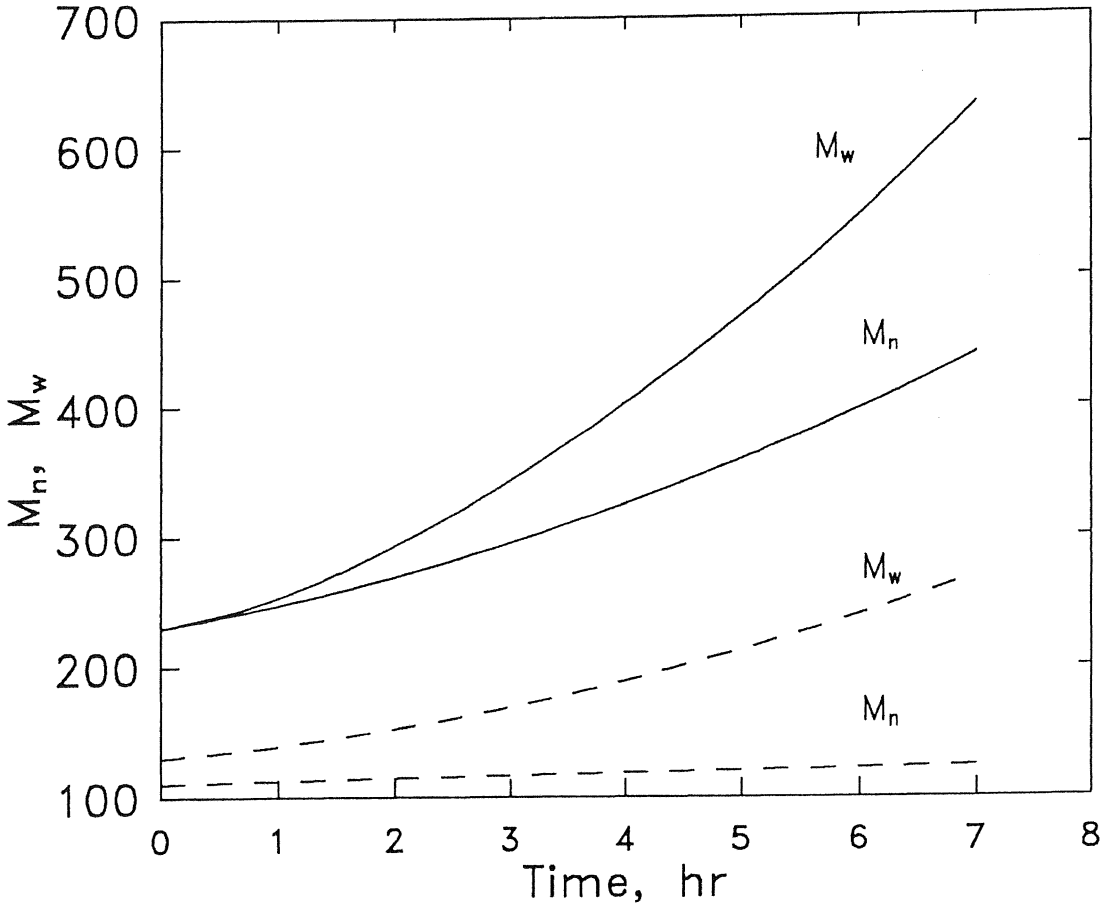

Fig. 9 : Variation of M_n and M_w with time. Dotted lines indicate average molecular weights incorporating epichlorohydrin. Solid lines indicate the variations excluding epichlorohydrin in the computation.

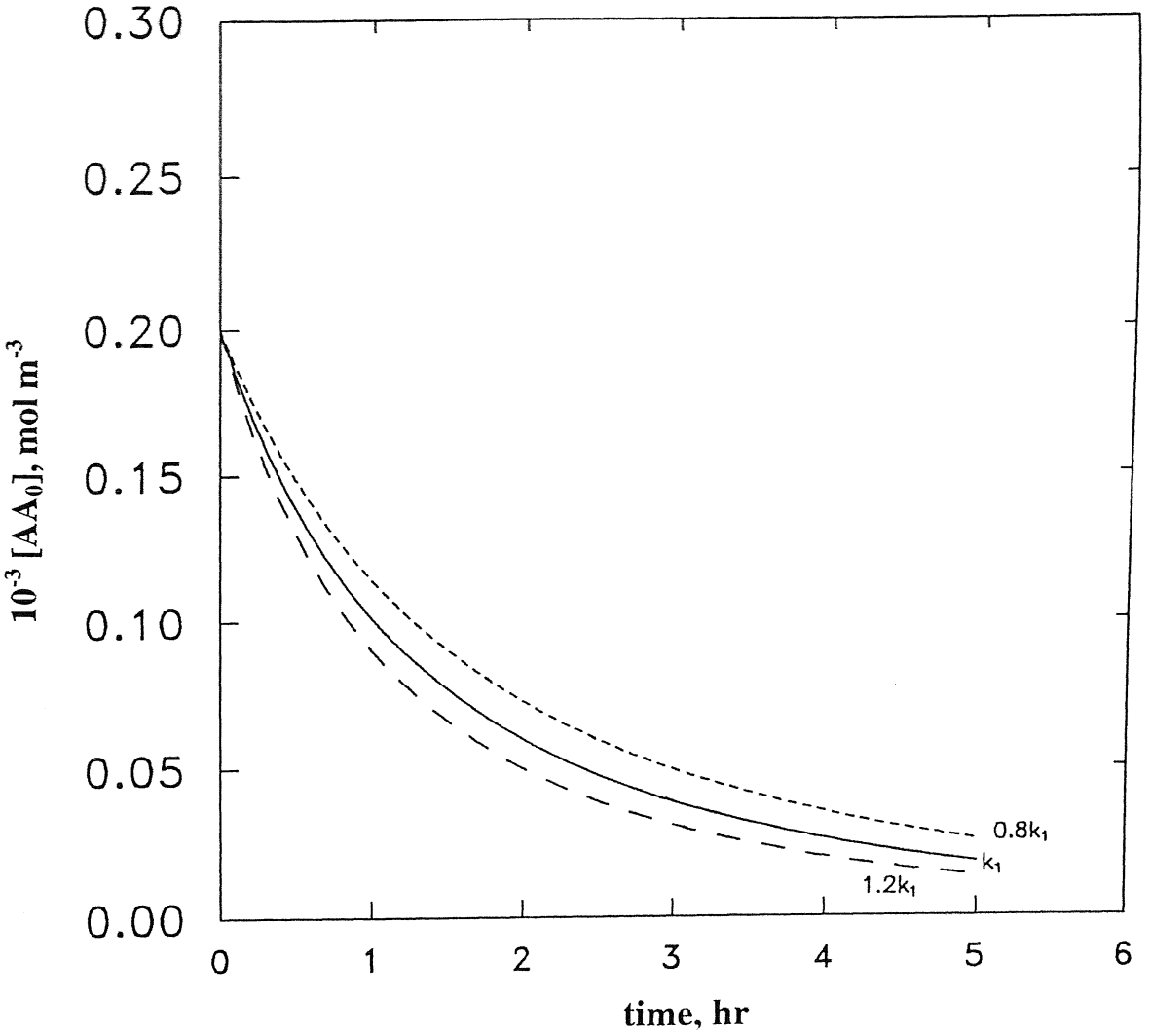

Fig. 10 : Sensitivity of the bisphenol A concentration to k_1.

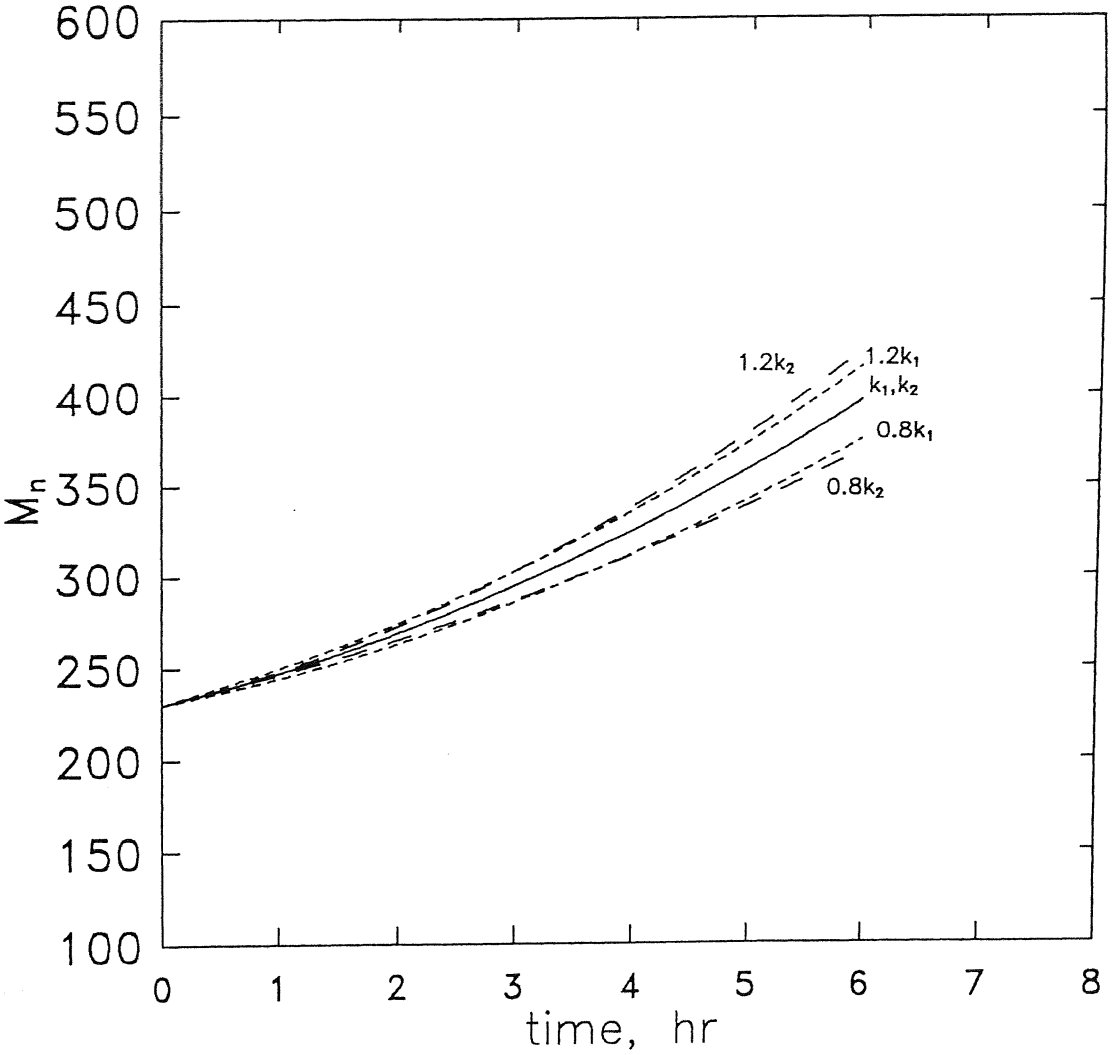

Fig. 11 : Sensitivity of M_n to k_1 and k_2. Epichlorohydrin excluded from computation of M_n.

is increased by about 20% (over the optimal or reference values). The sensitivity of M_n to the remaining three rate constants is much less. Similar conclusions are obtained for the sensitivities of M_w and PDI to variations in the rate constants (detailed plots can be provided on request). A word of caution may be mentioned at this stage. The kinetic scheme of Table 1 indicates that the main chain-lengthening steps are reactions 4 and 5. The relative insensitivity of M_n and M_w to variations in k_4 and k_5 could possibly be because of erroneous optimal values of these two rate constants (experimental data on M_n or M_w are not available, and the curve-fit using data on only the low molecular weight molecular species could bias our optimization against good values of k_4 and k_5).

An interesting simulation study is now made. Several industrial operations involve intermediate addition of NaOH. We run our simulation code to see the effect of sudden changes in NaOH concentration. The results so generated would give us some idea about the effects of NaOH addition in industrial epoxy reactors. Fig. 12 shows that higher M_n (and higher M_w and PDI) are obtained with intermediate addition of NaOH. A similar effect would be expected if we distill off water/epichlorohydrin in between (the concentration of NaOH would increase). It may be added that the probabilistic model of Ravindranath and Gandhi[4] cannot be used to provide such results and that our kinetic model is quite general. If we use appropriate values of the rate constants (corresponding to higher temperatures), and initial conditions typically encountered in the taffy or advancement processes, we could easily obtain the results of Ravindranath and Gandhi.[4] In fact, the latter model is really a subset of the present one. The probabilistic model,[4]

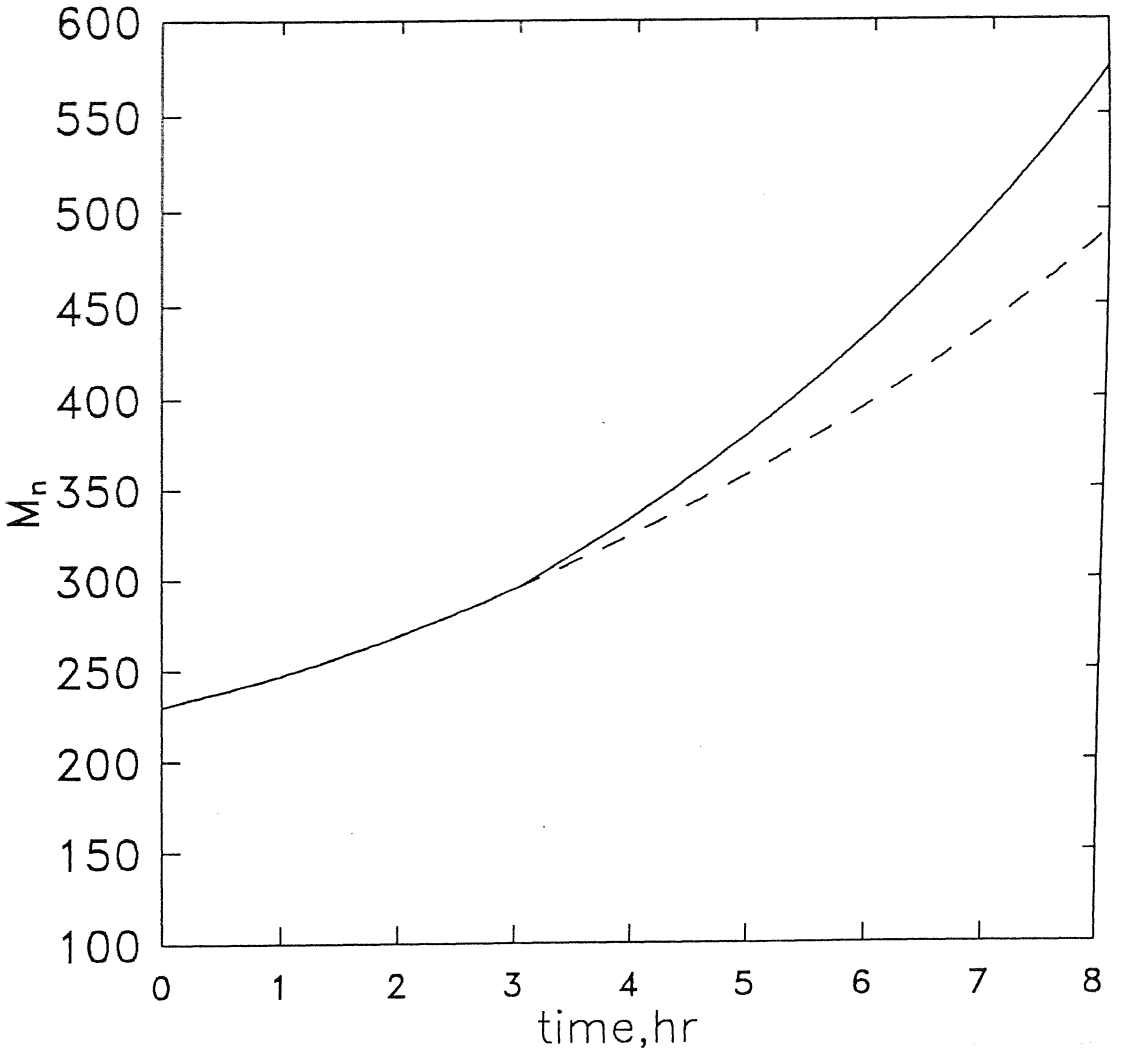

Fig. 12 : Solid curve indicates the variation of M_n with time, with [NaOH] concentration increased by 400 mol/m^3 above actual concentration at 3 hours. Dotted curve indicates the variation without any intermediate addition of NaOH.

however, is not easily amenable to account for physical effects usually present in industrial reactors, e.g., vaporization, intermediate addition, lack of good mixing, etc.

Chapter 4

Conclusions

A detailed kinetic model has been developed for epoxy polymerizations. The rate constants are curve-fitted using one set of experimental data available in the open literature. A sensitivity study has been carried out. The model incorporates the probabilistic model of Ravindranath and Gandhi[4] as a subset, but is far more powerful, as demonstrated by predictions for the case of intermediate additions of NaOH.

Chapter 5

Suggestions for Future Work

Experiments should be carried out at different temperatures to study the temperature effect on the model parameters and develop Arrhenius equations for the rate constants. Experimental data are required on concentrations of the different oligomeric species as well as on average molecular weights, so that the model parameters do not get biased by the former. Thereafter, the kinetic model developed here can be extended to apply for industrial reactors, and can be tested (or tuned) against industrial data. Optimization studies can then be performed.

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APPENDIX

Table A-1

Different Reactions Taking Place

$$AA_n + NaOH \xrightarrow{2k_1} AB_n + H_2O$$

$$AB_n + NaOH \xrightarrow{k_1} BB_n + H_2O$$

$$AE_n + NaOH \xrightarrow{k_1} BE_n + H_2O$$

$$AF_n + NaOH \xrightarrow{k_1} BF_n + H_2O$$

$$AB_n + EP \xrightarrow{k_2/H_2O} AF_n + NaOH$$

$$BB_n + EP \xrightarrow{2k_2/H_2O} BF_n + NaOH$$

$$BE_n + EP \xrightarrow{k_2/H_2O} EF_n + NaOH$$

$$BF_n + EP \xrightarrow{k_2/H_2O} FF_n + NaOH$$

$$AF_n + NaOH \xrightarrow{k_1} AE_n + NaCl + H_2O$$

$$BF_n + NaOH \xrightarrow{k_3} BE_n + NaCl + H_2O$$

$$EF_n + NaOH \xrightarrow{k_3} EE_n + NaCl + H_2O$$

$$FF_n + NaOH \xrightarrow{2k_3} EF_n + NaCl + H_2O$$

$$AB_n + AE_m \xrightarrow{k_4/H_2O} AA_{n+m+1} + NaOH$$

$$BB_n + AE_m \xrightarrow{2k_4/H_2O} AB_{n+m+1} + NaOH$$

$$BE_n + AE_m \xrightarrow{k_4/H_2O} AE_{n+m+1} + NaOH$$

$$BF_n + AE_m \xrightarrow{k_4/H_2O} AF_{n+m+1} + NaOH$$

$$AB_n + BE_m \xrightarrow{k_4/H_2O} AB_{n+m+1} + NaOH$$

$$BB_n + BE_m \xrightarrow{2k_4/H_2O} BB_{n+m+1} + NaOH$$

$$BE_n + BE_m \xrightarrow{2k_4/H_2O} BE_{n+m+1} + NaOH$$

$$BF_n + BE_m \xrightarrow{k_4/H_2O} BF_{n+m+1} + NaOH$$

(Table A-1 Continued... a)

Table A-1 : (Continued... a)

$$AB_n + EE_m \xrightarrow{2k_4/H_2O} AE_{n+m+1} + NaOH$$
$$BB_n + EE_m \xrightarrow{4k_4/H_2O} BE_{n+m+1} + NaOH$$
$$BE_n + EE_m \xrightarrow{2k_4/H_2O} EE_{n+m+1} + NaOH$$
$$BF_n + EE_m \xrightarrow{2k_4/H_2O} EF_{n+m+1} + NaOH$$

$$AB_n + EF_m \xrightarrow{k_4/H_2O} AF_{n+m+1} + NaOH$$
$$BB_n + EF_m \xrightarrow{2k_4/H_2O} BF_{n+m+1} + NaOH$$
$$BE_n + EF_m \xrightarrow{k_4/H_2O} EF_{n+m+1} + NaOH$$
$$BF_n + EF_m \xrightarrow{k_4/H_2O} FF_{n+m+1} + NaOH$$

$$AB_n + AF_m \xrightarrow{k_5} AA_{n+m+1} + NaCl$$
$$BB_n + AF_m \xrightarrow{2k_5} AB_{n+m+1} + NaCl$$
$$BE_n + AF_m \xrightarrow{k_5} AE_{n+m+1} + NaCl$$
$$BF_n + AF_m \xrightarrow{k_5} AF_{n+m+1} + NaCl$$

$$AB_n + BF_m \xrightarrow{k_5} AB_{n+m+1} + NaCl$$
$$BB_n + BF_m \xrightarrow{2k_5} BB_{n+m+1} + NaCl$$
$$BE_n + BF_m \xrightarrow{k_5} BE_{n+m+1} + NaCl$$
$$BF_n + BF_m \xrightarrow{k_5} BF_{n+m+1} + NaCl$$

$$AB_n + EF_m \xrightarrow{k_5} AE_{n+m+1} + NaCl$$
$$BB_n + EF_m \xrightarrow{2k_5} BE_{n+m+1} + NaCl$$
$$BE_n + EF_m \xrightarrow{k_5} EE_{n+m+1} + NaCl$$
$$BF_n + EF_m \xrightarrow{k_5} EF_{n+m+1} + NaCl$$

$$AB_n + FF_m \xrightarrow{2k_5} AF_{n+m+1} + NaCl$$
$$BB_n + FF_m \xrightarrow{4k_5} BF_{n+m+1} + NaCl$$
$$BE_n + FF_m \xrightarrow{2k_5} EF_{n+m+1} + NaCl$$
$$BF_n + FF_m \xrightarrow{2k_5} FF_{n+m+1} + NaCl$$

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where
m,n=0, 1, 2,...